

A theory of the normal and superconducting states of doped solid C₆₀

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We identify the 'stability of molecular singlets' (SMS) as an important feature of M_xC₆₀, and argue that it arises from the intramolecular carbon *pπ*-electron correlations and the consequent resonating valence bond (RVB) character of the 'two-dimensional' *pπ*-electron system of the C₆₀ molecule. Alternatively, SMS is shown to arise from the exchange of virtual triplet intramolecular excitons. SMS is modelled as an effective intramolecular pairing, resulting in a narrow band model with an effective negative Hubbard *U*, which explains the observed superconductivity as well as predicts anomalous boson metal like normal state properties. Disorder plays an important role and restricts superconductivity to a narrow range of *x* around 3. The narrowness of the conduction band puts limitations on the maximum attainable *T_c*.

IN a series of experiments C₆₀ molecule was synthesized¹, prepared in bulk², and was made a 'high-temperature' superconductor by alkali metal-doping^{3,4} (M_xC₆₀ with a *T_c* of 18 and 28 K for M=K and Rb). These findings are quite remarkable, and we suspect that there might be new physics in the normal and superconducting states, as in the case of the two-dimensional cuprate superconductors^{3,2}. We believe that the carbon *pπ*-bonding, which is so fundamental to a multitude of electronic processes in organic molecules and biological systems (starting from the valence bond resonance, singlet-triplet excitation splitting of benzene to the ill-understood long-range electron transfer in biomolecules), is also fundamental in this new carbon solid. Solid C₆₀, unlike the quasi two-dimensional graphite, is an insulator and a three-dimensional molecular solid. We will see, however, that it combines the physics of a finite two-dimensional resonating valence bond (RVB) state with three-dimensional narrow bands.

In this paper we develop and summarize some ideas which leads to a theoretical model and a scenario for the normal and superconducting state of M_xC₆₀.

The following are some of the key experimental results we use in building our model.

(i) The C₆₀ molecule is a sort of two-dimensional *pπ*-electron system⁵ with strong correlations and what might be described as an RVB ground state (with a small valence bond density modulation). In a host of organic compounds having very similar local carbon *pπ*-bonding, such as anthracene and pentacene⁶⁻⁸,

electronic correlations are known to be very important. Among other things, strong correlations manifest themselves experimentally in a large singlet-triplet excitation energy splitting ≈ 1 eV (indicating that the charge and spin behave differently) and the anomalous aromaticity properties. (ii) The undoped C₆₀ crystal, fullerene, is an insulating molecular crystal and metallicity results from doping. (iii) The normal state conductivity³ is rather small (500 S cm⁻¹) for K_xC₆₀ with a relatively small carrier concentration of $n \sim 10^{21}$ cm⁻³. (iv) Inverse photoemission studies⁹ show a rather narrow conduction band of width about 0.5 eV. This band appears to be derived from a three-fold degenerate *t_{1u}* molecular level; it can contain six electrons per site. (v) The coherence length is short and of the order of the size of C₆₀ molecule¹⁰. (vi) The possible absence of Pauli paramagnetism in the normal state EPR of the superconducting sample is suggested by some recent experiments¹⁰.

We argue that the electron correlation of the finite 'two-dimensional' C₆₀ molecule which gives it an RVB character plays a vital role by giving stable molecular singlets (SMS) even in the charged state of the C₆₀ molecule in the solid. This stability is explained by using the valence bond language and alternatively as an effective intramolecular antiferromagnetic coupling between the added electrons in the *t_{1u}* orbitals induced by exchange of molecular triplet excitons. A derivation of this antiferromagnetic coupling from the microscopics is sketched. *SMS implies a tendency for C₆₀ to be charged with even number of electrons on doping.* This can also be thought of as an on-site Cooper-pairing tendency, even though, the physics leading to this pairing is more collective in character. The relation of our collective pairing to Little's exciton-mediated pairing¹¹ is also discussed.

The above, together with the weak overlap between the *t_{1u}* orbitals of two neighbouring molecules, gives us three overlapping narrow bands with an effective negative Hubbard *U*. The attractive interaction, which we find is comparable to the narrow bandwidth, leads to enhanced pairing correlation even at room temperature in the normal state, thereby making the normal state a 'boson metal'. This means well-suppressed Pauli paramagnetism and marked departure from the Fermi liquid behaviour. We find that the one-particle energies of the *t_{1u}* orbitals are strongly

perturbed by the fairly unscreened dopant potential. This makes the strength of the disorder potential, arising from the dopant disorder, comparable to the conduction bandwidth and causes localization at the Fermi level over a wide range of x .

We suggest that a narrow region around $x=3$ escapes disorder and our model predicts superconductivity in this region. Since we have a non-retarded on-site attractive interaction we find that there are limitations on the maximum value of T_c that is attainable. At the end we make certain predictions based on our model and discuss the relevance of electron-lattice coupling in these systems.

The model and determination of the parameters

The molecule C_{60} is a carbon $p\pi$ -bonded system with a truncated icosahedral shape. The orbitals close to the Fermi level are the p_z orbitals. They strongly hybridize to form the 60 single-particle molecular orbitals¹² spread over an energy of about 15 eV. The Fermi level of the molecular solid C_{60} (an fcc crystal) lies between a set of filled narrow bands formed by the five-fold degenerate g_{1u} orbitals and an empty set of narrow bands formed by the three-fold degenerate t_{1u} orbitals. The gap is about 2 eV. The t_{1u} orbitals can be chosen to transform as x , y and z , just like the atomic p_z orbitals.

We have suggested¹³ that the narrow conduction bands should resemble the (well isolated) $4p$ hole-like valence band of the fcc solid Krypton on account of its p -character. This turns out to be mostly true as shown by a recent band structure calculation¹⁴. There are three overlapping bands. Two almost-degenerate narrower bands of width 0.2 eV overlapping at the top of a narrow band of width 0.5 eV. All the bands are degenerate at the Γ point.

We argue that the low energy physics is governed by the following conduction band Hamiltonian

$$H = \sum t_{ab} c_{ia\sigma}^\dagger c_{jb\sigma} + h.c. + I \sum \mathbf{S}_{ia} \cdot \mathbf{S}_{ib} + U \sum n_{ia} n_{ib} + U_d \sum n_{ia\uparrow} n_{ia\downarrow}, \quad (1)$$

$$\text{where } \mathbf{S}_{ia} = c_{ia\alpha}^\dagger \vec{\sigma}_{\alpha\beta} c_{ia\beta}. \quad (2)$$

Here c 's are the electron operators, a , $b=1, 2$ and 3 stand for the three degenerate t_{1u} orbitals at any site i . The hopping matrix elements t_{ab} are assumed to be non-zero only between nearest-neighbours and are obtained from a tight-binding fit to the actual band structure. The second term on the right represents the exchange coupling I between two electrons that occupy orbitals a and b of the i th molecule. The terms U_d and U represent the Coulomb repulsion between two electrons occupying the same or two different t_{1u} orbitals of a molecule.

We have estimated the interaction parameters by using various arguments which we present below very

briefly. The most crucial parameter is $U - \frac{3}{2}I$. This is the energy gained in the transition $C_{60}^{1-} C_{60}^{1-} \rightarrow C_{60}^0 C_{60}^{2-}$ of two neighbouring molecules in a solid. Here the two excess electrons in C_{60}^{2-} ion occupy two distinct degenerate t_{1u} orbitals in a spin-singlet state.

The parameters U , U_d and I will be modified for the transmitter like $C_{60}^{3-} C_{60}^{3-} \rightarrow C_{60}^{2-} C_{60}^{4-}$. Moreover we will concentrate on the region x around 3. Also, there is an approximate symmetry about $x=3$ in our model.

The SMS that we identify depends on the parameter $U - \frac{3}{2}I$. If it is negative, in spite of the Coulomb repulsion, the above-mentioned transition will take place and stabilize the molecular singlets. Also, notice that SMS is independent of the diagonal Hubbard parameter U_d .

We find that the diagonal Hubbard parameter U_d is of the order of the bandwidth. And the off-diagonal parameter U , becomes small when the Madelung energy as well as screening effect are included. We will hence assume this to be zero.

The most crucial parameter determining SMS is thus I . It gets contributions from the Hund's rule (ferromagnetic) exchange, the π -electron correlation and the lattice effects. We will argue that the π -electron correlation contributes dominantly. We give two methods of estimating this (i) valence bond arguments, and (ii) triplet-exciton exchange approach. The gist of valence bond approach¹³ is as follows. It is well known that carbon $p\pi$ -bonded systems are described very well as resonating valence bond (RVB) states^{15,16}. In particular they are short-range RVB states. As the size of the molecule becomes larger there are valence bond density modulations.

The valence bond character (i.e. suppression of polar fluctuations and dominance of singlet homo-polar configurations) has its origin in strong correlations in the tight-binding carbon $p\pi$ -electrons of the C_{60} molecule. In a PPP-Hubbard model^{8,17} description the effective Hubbard U is of the order of 5 eV. A phenomenological t - J model description¹³ can also be given with a $t \approx 2.5$ eV and a $J \approx 0.8$ eV.

The valence band energy J is easily estimated⁸ from the triplet-exciton energy E_T . For C_{60} the experimental value of E_T is ≈ 1.6 eV, making $J \approx 0.8$ eV. The value I is different from J . Moreover, the singlet-triplet exciton splitting (≈ 0.5 eV) observed³³ in C_{60} also emphasizes the importance of correlations.

The fact that we have a two-dimensional tight-binding system with 60 sites makes the valence bond correlations very important. Our SMS hypothesis expresses the tendency of the 2-d RVB system not to have any unpaired spins. Any unpaired spin means a presence of a broken valence bond and an exchange energy increase of the order of J . There is a close connection¹⁸ of our SMS hypothesis with the Lieb-Mattis theorem⁹ for one-dimensional systems. Also,

recent numerical calculations of large U Hubbard models on finite two-dimensional lattices as well as finite clusters exhibit chemical potentials which are larger for even electron singlet ground states rather than the odd electron states.

According to our valence bond picture, when a pair of electrons is added to a neutral molecule the entire π -electron systems adjusts itself to have local singlet character. This is achieved to a large extent, by having two real doubly occupied sites (doublons^{20,22}) which are well separated (because of Coulomb repulsion) and delocalized among the resonating singlets. Including the string energy that arises from the presence of valence bond modulation we find that I is in the range 0.1 to 0.4 eV.

The physics of our calculation of I is similar to a calculation of the binding energy of two charged solitons in *cis*-polyacetylene, even though the topology in the present case is different. Also, we find that the electron-electron²² rather than the electron-phonon interaction contribute dominantly to I .

Another way of arguing how the exchange energy J wins over the Coulomb energies in the large C_{60} molecule is as follows. Electrostatic energies like U and U_d decrease as $\frac{1}{R}$, where R is the size of the molecule. On the other hand, the valence band energies J decrease at a much slower rate³³. Between benzene and C_{60} the triplet exciton energy ($\approx 2J$) has a marginal decrease from 2.5 to 1.6 eV.

In another approach we have estimated I by using the exchange of virtual triplet exciton. The C_{60} molecule has a triplet and the singlet exciton has two lowest energy excitations. We find that the coupling of the added electron to the triplet exciton is the strongest. The origin of the polarization energy which we get when we add extra charges can be viewed to arise from the virtual excitations of these excitons. When two charges are added they exchange these virtual excitons.

Exchange of singlet excitons does not give rise to any spin-dependent polarization energy. It reduces the overall electrostatic repulsions. On the other hand, the exchange of triplet excitons favours singlet pairing. We also find that the strongest coupling of the electrons is to the triplet excitons.

Starting from the PPP-Hubbard Hamiltonian we have found¹³ the interaction Hamiltonian (written in a manifestly spin rotation invariant form) between an electron in a t_{1u} orbital and the lowest energy singlet exciton to be

$$\frac{2}{3}U_p \frac{1}{\sqrt{60}} c_{ax}^\dagger \bar{\sigma}_{\alpha\beta} c_{ax} \cdot \vec{S}_0, \quad (3)$$

where $a=1, 2$ and 3 denotes the three t_{1u} states and \vec{S}_0 is the operator for the lowest triplet state of the C_{60} molecule. Here U_p is the Hubbard U for the carbon π -orbital.

By a simple second order perturbation theory we find an effective interaction between electrons in the orbital a and b :

$$I c_{ia\alpha}^\dagger \bar{\sigma}_{\alpha\beta} c_{ia\beta} \cdot c_{ib\alpha'}^\dagger \bar{\sigma}_{\alpha'\beta'} c_{ib\beta'} = I \mathbf{S}_{ia} \cdot \mathbf{S}_{ib} \quad (4)$$

$$\text{and } I = \frac{3}{4} \left(\frac{2}{3} \frac{U_p}{\sqrt{60}} \right)^2 \frac{1}{E_T}. \quad (5)$$

When we choose $E_T \approx 1$ eV and the $U_p \approx 11$ eV we get this exchange coupling $I \approx 0.3$ eV. When we add three or more electrons by the arguments given above the lowest spin state will be always stabilized.

Even though our exciton exchange approach looks similar to Little's mechanism¹¹, there are some important differences. The excitons are intramolecular in nature and live in the same region where the conduction electrons live. Hence our mechanism escapes the criticism of Inkson-Anderson²²: that is, the reduction in screening which occurs when the active electron pairs tunnel into the interaction region does not arise in our case. The two added electrons are part of the carbon $p\pi$ -electrons and the triplet exciton is a collective excitation of this system. More importantly, we believe that the singlet stabilization process, even though has two explanations, the first one in terms of valence bond is more natural and captures the essential physics of these carbon $p\pi$ -bonded system.

Effects of disorder

The solid $M_x C_{60}$ is not a periodic solid for a general value of x : even though the molecules form a periodic lattice we expect M to be distributed to some extent randomly, particularly when x is not close to one of the commensurate values like 2, 3, 4 and 5. Experimentally we do not know the detailed solubility of M as a function of x . Even when $x=2$ it is easily seen that there are several ways of distributing M , the dopant atoms in the solid, thereby giving rise to many nearly degenerate disordered configurations of M .

In a disordered tight-binding system an important parameter is the ratio of the bandwidth to the strength of disorder. As mentioned earlier our bandwidth is very small and is of the order of 0.5 eV. To get an idea of the strength of disorder, we would like to estimate the change in energy of an electron in one of the t_{1u} orbitals due to an excess potassium nearby:

$$\delta E \approx \frac{e^2}{\epsilon r_0} \approx 0.5 \text{ eV}, \quad (6)$$

where $\epsilon \approx 5$ is the dielectric constant²¹ at short distances of the order of the size of the molecule and r_0 is a distance of the order of 7 Å. This energy is comparable to the bandwidth. If there are two excess potassium atoms near a molecule we expect the energy

to change by a factor of 4, i.e. ≈ 2 eV. Even if we include some higher order screening, the strength of the potential fluctuation is not reduced considerably.

Thus we are in a strong disorder limit. This disorder is important particularly when x is close to 0 or 6. It is likely that, until $x \approx 2$, the disorder is significant and states at the Fermi level in the lowest band, namely the broad band, are localized. Beyond $x=2$ the potential fluctuations are smoothed out to some extent because of the screening from the filled localized states. Moreover, when we reach higher commensurate values like $x=2$ and 3 there are good periodic arrangements of the dopants which will reduce the disorder. We should also point out that the negative U that we have talked so far also helps in localizing the states in the lowest broad band.

Superconductivity for $x \approx 3$ and limits on T_c

Since the experimentally observed interesting region seems to be around $x=3$, we will concentrate on the two nearly degenerate narrow bands that are close to the Fermi level (Figure 1). It is true that disorder remains finite even in this range of x . The fact that superconductivity is observed in this region means that the disorder is not sufficient to destroy it.

Before we analyse our model for superconductivity several things can be inferred. The pairing energy is of the order of the bandwidth. Hence we are deep into the real space-pairing regime. Because any reasonable temperature like room temperature is very small compared to the pair-binding energy I which is of the order of 1000 to 2000 K.

A BCS analysis of eq. (1) is easily performed if we rewrite

$$S_{ia} \cdot S_{ib} = -b_{iab}^\dagger b_{iab} + \frac{1}{4} n_{ia} n_{ib} \quad (7)$$

and factorize the attractive interaction as

$$b_{iab}^\dagger b_{iab} \rightarrow \langle b_{iab}^\dagger \rangle b_{iab} + \text{h.c.} \quad (8)$$

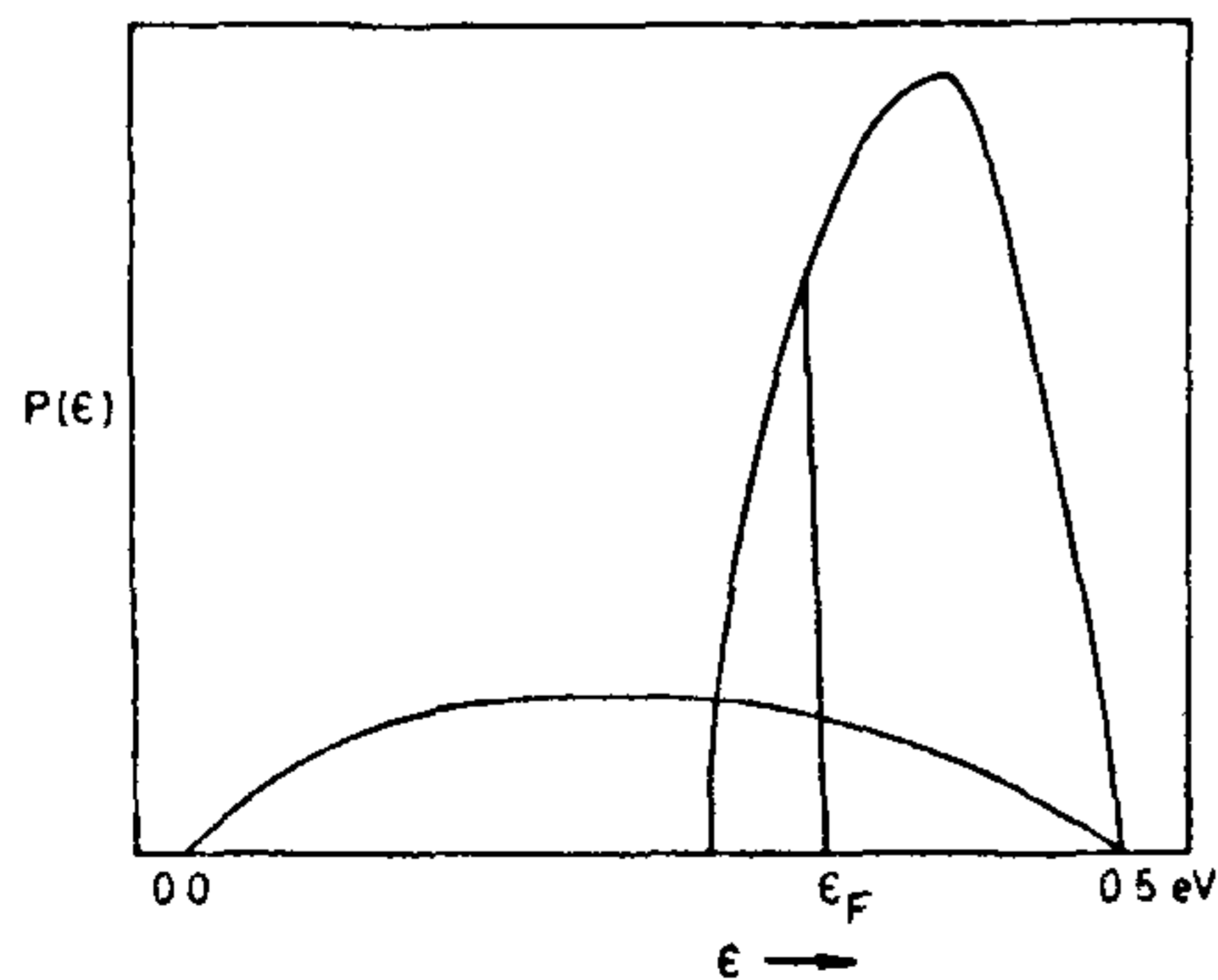


Figure 1. Schematic diagram of density of states of the t_{1u} bands—two nearly degenerate narrower bands overlapping with another narrow band. The Fermi level ϵ_F is for a filling $x \approx 3$.

The details of the results will be published later¹³.

For the moment we will concentrate on qualitative features that follow by making several simplifying assumptions and trying to get a feel for the value of T_c in particular. Firstly, in our model, even though there are three bands, there is a two-particle state on a molecule that is favoured. This state corresponds to two electrons occupying the two separate Wannier orbitals 1 and 2 of the two nearly degenerate top narrow bands in a singlet state. The Wannier orbital 3 of the broad band is almost filled with two electrons and is deep from the Fermi level. The other two degenerate states in which the two electrons doubly occupy any one of the Wannier orbitals 1 and 2 have higher energy. In this sense it is like a one-band model with a width approximately equal to the width of the two top narrow bands (≈ 0.2 eV). We will also look at the results for a cubic lattice. We have checked that this does not change the results qualitatively.

This negative- U one-band Hubbard model has been studied²⁵ in great detail in the context of Anderson's negative- U bipolaron²⁶ model of superconductivity²⁷ as well as general bipolaron superconductivity in narrow-band systems²⁵. Several remarks are in order about the phase diagram (Figure 2). Firstly we are deep into the real-space pairing regime. For the value of parameters that we have it is easily seen from the graph that we have a $T_c \approx 70$ K. The interesting fact is that when the binding energy exceeds the bandwidth the T_c tends to decrease but rather slowly. The maximum T_c occurs when the binding energy is about half the bandwidth. This is a kind of universal number within the BCS approximation and also indicates most importantly that there will be a saturation in value of T_c within the one band short range non-retarded attractive interaction model. From the mean field theory we get an approximate expression for the

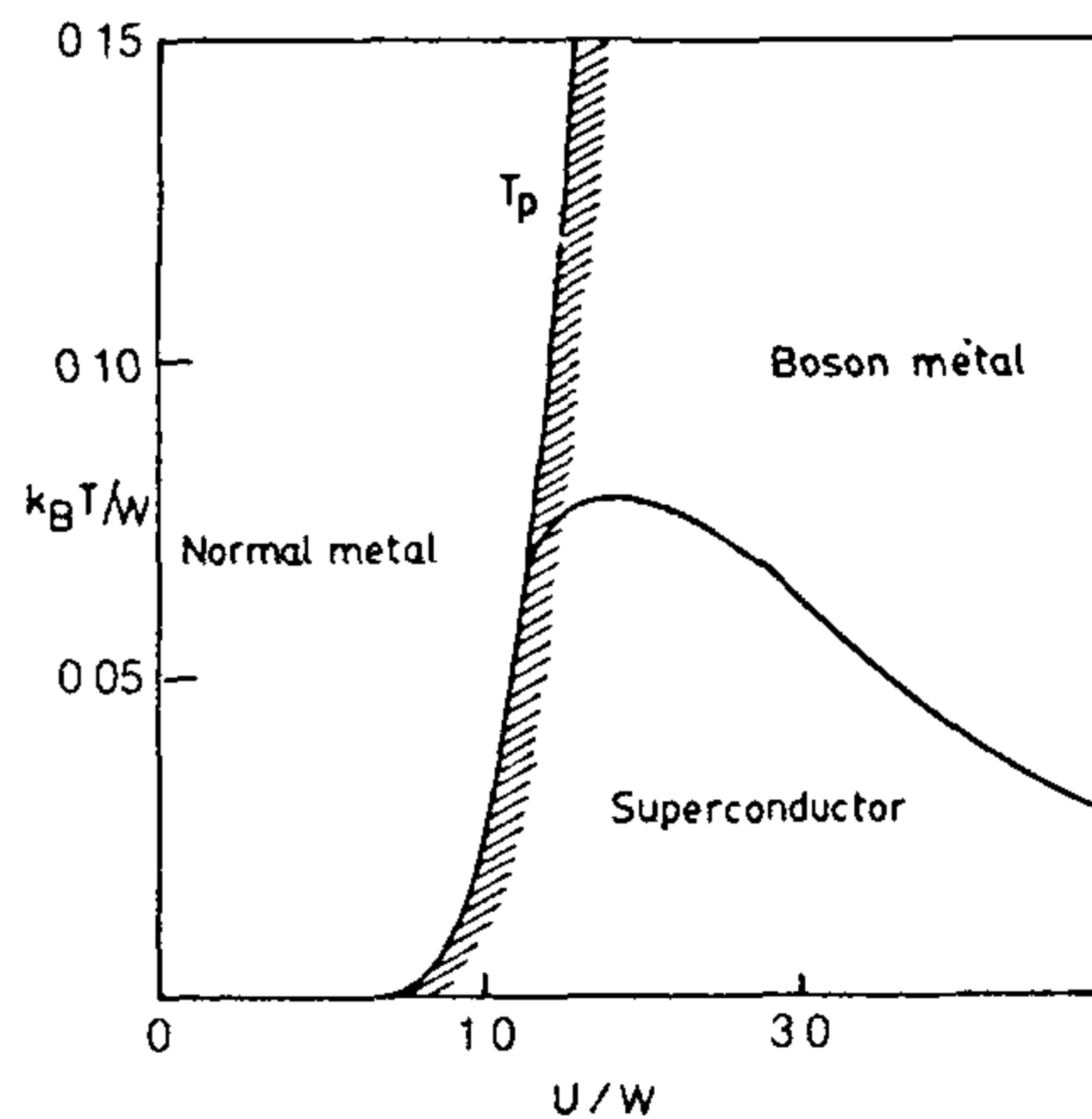


Figure 2. The $k_B T - U$ phase diagram in units of W for a half-filled negative- U Hubbard model (cf ref. 25). T_p is the pair-breaking temperature.

maximum value of T_c

$$\frac{k_B T_c^{\max}}{2W} \approx 0.035 \quad (9)$$

in terms of the bandwidth $2W$. For our bandwidth $k_B T_c^{\max} \approx 60$ K. Even if we are optimistic and take the bandwidth of the broad band, the maximum $k_B T_c \approx 200$ K. Fluctuation effects, the fcc nature of our lattice and the unscreened short-range Coulomb interaction will further reduce the phase boundary in the phase diagram. From that point of view the saturation value that we have given is more like an upper bound. We are trying to understand the saturation behaviour and its possible consequence to the new class of carbon superconductors and other organic superconductors.

We would also like to point out that within our model the source of difference between the T_c for K and Rb doping⁴ could arise either because of the difference in the bandwidth or U or disorder. At the moment we are unable to pin point the cause.

It is obvious that owing to the short coherence length and the expected large London penetration length ours is a type II superconductor. The fact that we have real-space pairing has some interesting consequences for the electromagnetic properties and the behaviour of energy gap. It is found²⁵ that some of the properties are qualitatively different from the BCS behaviour: the energy gap is very weakly temperature-dependent all the way up to T_c . We expect non-standard behaviour of the detailed temperature dependence of the penetration length $\lambda_H(T)$ and $H_c(T)$, as was already found in the low-density regime^{25a}.

Some comments on the normal state

In ordinary superconductors the normal state is a Fermi liquid, perhaps with some pairing fluctuation. Even in the well-known strong-coupling superconductors a Fermi liquid description works remarkably well. The pairing fluctuation leads to suppression of the wave function renormalization of the electron close to the Fermi surface. This is never catastrophic. In our case, the scale of binding is large compared to the room temperature and hence the normal state is more like a charged Bose liquid in the normal state. This normal state is anomalous and in some sense can be thought to be governed by a fixed point which is not a Fermi liquid fixed point. It is the fixed point corresponding to a non-superfluid Bose liquid. Even though there is no fundamental symmetry difference between the non-superfluid Bose fluid and the Fermi fluid at finite temperature, in practice the description is more easy and more meaningful in terms of one rather than the other.

We expect anomalies very similar to the one that is

observed in the cuprate superconductors. Even though we do not have a spin charge decoupling situation here, there are certain generic features which come with the break down of Fermi liquid character. These generic features follow simply from the fact that an electron injected at k_F will decay into a whole lot of low energy excitations. That is the electron will give away almost all of its spectral weight to other many-body collective excitations.

We expect the imaginary part of the electron self-energy to have the form

$$\text{Im} \sum_{k_F}(\omega) \propto \omega^\alpha, \quad (10)$$

where α is an exponent close to unity. This is the form that was suggested by Anderson²⁸ and others²⁹ with $\alpha=1$ to explain some of the normal state phenomenology of the cuprate superconductors. This has the well-known consequence of anomalous normal state tunnelling conductance $g(V) \approx g_0 + g_1 V$, large deviation from the normal temperature dependence in resistivity $\rho \approx aT^\gamma$, where γ is close to unity, and the anomalous electronic Raman scattering, etc.

We expect strong suppression of the Pauli paramagnetic susceptibility arising from the real-space pairing. In this sense this system will be very different from the cuprate superconductors, where in the normal state the low energy spinon excitations do exist and they contribute to Pauli paramagnetism. In fact, recent experiments involving EPR measurements¹⁰ do indicate this possibility. Thus the NMR relaxation will also be anomalous, owing to the absence of free spins close to the Fermi surface.

In the real-space regime the specific heat in the superconducting and normal region is expected to have strong deviation from the conventional BCS behaviour. For example, $C_v \approx T^3$ crossing over to $T^{3/2}$ has been found in some approximate analysis. As mentioned in ref. 25, the high density limit of the real-space pairs has not been well-understood.

When superfluidity in an interacting system is suppressed by disorder effects we get a Bose glass. This problem has been studied in the recent past to understand the behaviour of superfluid helium-4 in vycar glass. We have a situation which has two important differences from helium-4: (i) the bandwidth is bounded, and, in fact, we have a very narrow band, and (ii) the Coulomb interaction.

Anderson localization of one-electron states in the presence of disorder is well known. When we have a strong local pairing, the two-electron states are localized in space. Since pair tunnelling bandwidth is narrower, we expect the effect of disorder even stronger.

From this point of view the entire range of x except for values close to 3 and other commensurate values we expect a Bose glass¹⁴. Because the pair bandwidth is

sufficiently small compared to the strength of disorder. The experimental consequences of this anomalous phase is being studied¹⁸.

Effects of coupling to dynamical molecular and lattice distortions

In a one-electron picture, a single-spherical C_{60} molecular ion with a partly occupied t_{1u} level ($n < 6$) is Jahn–Teller unstable against a symmetry-lowering distortion. Tunnelling between equivalent distortions can further dynamically re-establish the full icosahedral symmetry. A dynamical Jahn–Teller state of this type can thus achieve a gap in its electronic spectrum, and a maximally paired electron configuration without any static lattice symmetry breaking. This kind of outcome is in a way remarkably similar to that produced by a positive antiferromagnetic spin–spin interaction I , introduced earlier as a purely electronic correlation effect. In this sense coupling to symmetry-breaking molecular vibrations may be seen simply as providing an additional reinforcing effect for singlet formation. This is at the heart of the Jahn–Teller bipolaron mechanism³⁰. In the present case, the Coulomb correlation and this lattice effect seem to go hand in hand. This is to be contrasted with the conventional BCS–Macmillan–Eliashberg superconductors, where the Coulomb effects play against the lattice effects.

Whether the lattice effect dominates or the correlation dominates in establishing superconductivity in M_xC_{60} is a matter of numbers. Here we would like to add several qualitative but important considerations, as to why we do not believe lattice coupling to constitute the really key ingredient in this case. First of all, as always, strongly coupled lattice polaron and bipolaron superconductivity is hampered by large mass enhancement, which cuts off severely the maximum T_c attainable. On the contrary, a large electronic I as argued here may renormalize the single-particle hopping but not pair hopping. In this sense the lattice is a dangerous ally. Secondly, the estimated Jahn–Teller splittings and more generally lattice-induced splittings are minute even relative to a small one-electron bandwidth of 0.5 eV, amounting to a reduction of the on-site Coulomb repulsions perhaps by about 0.05 eV. Thus the effect is only a small fraction of the effective U that we have estimated using the electron correlations.

The next is the intramolecular optical phonon, which, for example, is used in discussing the physics of polyacetylene by Su, Schrieffer and Heeger^{17,31}. We have also studied¹³ the soliton mechanism of Su, Schrieffer and Heeger appropriately modified for the topology of C_{60} molecule and find that it goes along the same way as our correlation mechanism and adds a

small component to the low-spin stabilization. Hence we believe that the detailed energetics and physics is controlled by Coulomb interaction and the associated exchange effects rather than by electron–phonon interaction in small system like ours. This has been well demonstrated^{8,17,22} by quantum chemical calculations in carbon π -bonded molecules as well as infinite systems such as polyacetylene.

Conclusions

The following are certain predictions of our modelling and mechanism: (1) C_{60} ions in the gaseous phase should have low-spin ground state with the splitting from the next high-spin state by about 0.1 to 0.4 eV. Experimental as well as numerical attempts to understand this will be welcome. (2) The coherence length will be of the order of the size of the molecule. There has been some recent experimental report suggesting this also. (3) Superconductivity will be absent for x in the region ≈ 0 to 2 and 4 to 6. (4) Maximum T_c will be observed for x around 3. (5) The normal state is anomalous with near-absence of free spins: consequently, i) no Pauli paramagnetism, ii) anomalous tunnelling conductance, iii) flat Raman scattering intensity at low energies. Recent EPR measurements¹⁰ suggest absence of Pauli paramagnetism.

In conclusion, we have discussed some aspects of the low-energy properties of M_xC_{60} . The intramolecular correlation which is also responsible for the RVB character has been argued to be responsible for the on-site pairing. This has also been explained using the triplet-exciton exchange approach. In the interesting region around $x=3$ we have an effective two-band Hubbard model with a negative U . Using the known results of the one-band Hubbard model we argue that there will be a saturation in value of T_c within our model. Fluctuations and unscreened part of the short-range Coulomb interaction will further reduce this maximum value of T_c . Because the pair energy is comparable to the bandwidth and large compared to the room temperature, the low-temperature transport and thermodynamic and magnetic properties will be dominated by pair fluctuations.

1. Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F. and Smalley, R. E., *Nature*, 1985, 318, 162.
2. Krätschmer, W., Lamb, L. D., Fostiropoulos, K. and Huffman, D. R., *Nature*, 1990, 347, 354.
3. Haddon, R. C., Hebard, A. F., Rosseinsky, M. J., Murphy, D. W., Duclos, S. J., Lyons, K. B., Miller, B., Rosamilia, J. M., Fleming, R. M., Kortan, A. R., Glarum, S. H., Makhija, A. V., Muller, A. J., Eick, R. H., Zahurak, S. M., Tycko, R., Dabbagh, G. and Thiel, F. A., *Nature*, 1991, 350, 320.
4. Hebard, A. F., Rosseinsky, M. J., Haddon, R. C., Murphy, D. W., Glarum, S. H., Palstra, T. T. M., Ramirez, A. P. and Kortan, A. R., *Nature*, 1991, 350, 600, Rosseinsky, M. J., Ramirez, A. P., Glarum, S. H., Murphy, D. W., Haddon, R. C., Hebard, A. F.,

- Palstra, T. T. M., Kortan, A. R., Zahurak, S. M. and Makhija, A. V., *Phys. Rev. Lett.*, 1991, **66**, 2830.
5. The carbon sp^2 hybridization easily leads to a local two-dimensional (planar) character in organic molecules.
 6. McGlynn, S. P. *et al.*, *Molecular Spectroscopy of the Triplet State*, Prentice Hall, New Jersey, 1969.
 7. Silinsh, E. A., *Organic Molecular Crystals*, Springer Series in Solid State Science, No. 16, Springer, New York, 1980.
 8. Edward, C. Lim, V. (ed.), *Excited States*, Academic Press, 1982, Vol. 6, First article.
 9. Weaver, J. H., José Luís Martins, Komeda, T., Chen, Y., Ohno, T. R., Kroll, G. H., Troullier, N., Haufler, R. E. and Smalley, R. E., *Phys. Rev. Lett.*, 1991, **66**, 1741; Benning, P. J. *et al.*, preprint, April 1991.
 10. Haddon, R. C., private communication.
 11. Little, W. A., *Phys. Rev.*, 1984, **A134**, 1416; Ginzburg, V. L., *Sov. Phys. JETP*, (Engl. Transl.) 1965, **20**, 1549.
 12. Haymet, A. D. J., *Chem. Phys. Lett.*, 1985, **122**, 421; Haddon, R. C., *Chem. Phys. Lett.*, 1986, **125**, 459; Disch, R. L., Schulman, J. M., *Chem. Phys. Lett.*, 1986, **125**, 465; Fowler, P. W., Woolrich, J., *Chem. Phys. Lett.*, 1986, **127**, 78; Ozaki, M. and Takahashi, A., *Chem. Phys. Lett.*, 1986, **127**, 242; Satpathy, S., *Chem. Phys. Lett.*, 1986, **130**, 545.
 13. Baskaran, G. and Tosatti, E., to be published
 14. Bassani, F. and Pastori Parravicini, G., *Electronic Structure and Optical Transitions in Solids*, Pergamon Press, New York, p. 139, and references therein; Saito, S. and Oshiyama, A., *Phys. Rev. Lett.*, 1991, **66**, 2665.
 15. Pauling, L., *The Nature of the Chemical Bond*, Oxford University Press, London, 1963.
 16. Coulson, C. A., *Valence*, Oxford University Press, London, 1965.
 17. Yu Lu, *Solitons and Polarons in Conducting Polymers*, World Scientific, Singapore, 1988, and many of the papers reprinted there, especially those dealing with the effect of Coulomb interactions.
 18. Baskaran, G., to be published.
 19. Leib, E. and Mattis, D., *Mathematical Physics in One Dimension*, Academic Press, New York.
 20. Kivelson, S., Rokhsar, D. and Sethna, J., *Phys. Rev.*, 1987, **B35**, 8865.
 21. Anderson, P. W., Baskaran, G., Zou, Z. and Hsu, T., *Phys. Rev. Lett.*, 1987, **58**, 2790.
 22. Ovchinnikov, A. A., Ukrainskii, I. I., Kventsel, G. V., *Sov. Phys. Usp.*, 1973, **15**, 575.
 23. Inkson, J. C. and Anderson, P. W., *Phys. Rev.*, 1973, **B8**, 4429; Allender, D., Bray, J. and Bardeen, J., *Phys. Rev.*, 1973, **B8**, 4433.
 24. A note about the dielectric constant. We have used a dielectric constant of $\epsilon=5$, which is estimated using the plasma frequency of the π -electron system as well as the overall gap from the optical absorption experiment. This value is also very close to the value in graphite, which is very similar to C_{60} as far as local electronic character is concerned. As the potassium concentration increases the polarizability of the potassium will also contribute and we expect it to increase, Academic Press, New York, 1966.
 25. Micnas, R., Ranninger, J. and Robaszkiewicz, S., *Rev. Mod. Phys.*, 1990, **62**, 113.
 26. Anderson, P. W., *Phys. Rev. Lett.*, 1975, **34**, 953.
 27. Chakravarti, B. K., *J. Phys. Lett.*, 1979, **B40**, L99.
 28. Anderson, P. W., *Phys. Rev. Lett.*, 1990, **64**, 1839; **65**, 2306.
 29. Varma, C. M., Littlewood, P. B., Schmitt-Rink, S., Abrahams, E. and Ruckenstein, A. E., *Phys. Rev. Lett.*, 1989, **63**, 1996.
 30. Johnson, K. H. *et al.*, preprint.
 31. Su, W. P., Schrieffer, J. R. and Heeger, A. J., *Phys. Rev.*, 1980, **B22**, 2099.
 32. Anderson, P. W., *Science*, 1987, **235**, 1196.
 33. Arbogast, J. W. *et al.*, *J. Phys. Chem.*, 1991, **95**, 11.

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Steric and rotational constraints in the X-ray structure of the antimalarial drug amodiaquine

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In the crystal structure of the antimalarial drug amodiaquine, the bonds linking the quinoline and the phenyl groups show partial double-bond character. The partial double-bond character of the two exocyclic bonds, together with stereochemical constraints, reduce flexibility of the two ring systems of the molecule. The dihedral angle between the two ring planes is lowest compared to those in the antileukaemic drug amsacrine and its derivatives. CPK-modelling studies suggest the way amodiaquine can bind to DNA. Stacking interaction

between the quinoline and phenyl groups of independent molecules and the hydrogen-bond network stabilize the crystal structure.

AMODIAQUINE, 4-[(7-chloro-4-quinolinyl)amino]-2-[(diethylamino)methyl]phenol, an analogue of the widely used antimalarial drug chloroquine, is also used for treating malaria. It has some structural resemblance with the antileukaemic drug amsacrine (AMSA), where