

been received very well by the scientific community who have felt that the review talks and discussions were of consistently very high academic standard. They have also felt that these sessions provided a unique opportunity to the senior and young researchers to exchange ideas about their work on the same platform. DST has received several requests from scientists to organize more brain storming sessions even

on the subject areas already covered and from young researchers to participate in more than one session. The exercise has also helped DST to generate some good projects.

Detailed reports and recommendations of the brain storming sessions, including lists of participants, are available with the Department of Science and Technology, New Delhi.

We are grateful to the past and

present chairmen and members of the programme advisory committee on plant sciences, chairmen of the brain storming sessions, experts and participants for their advice and help in organizing these sessions and for making them successful by their participation.

Parveen Farooqui, Department of Science and Technology, New Delhi.

RESEARCH NEWS

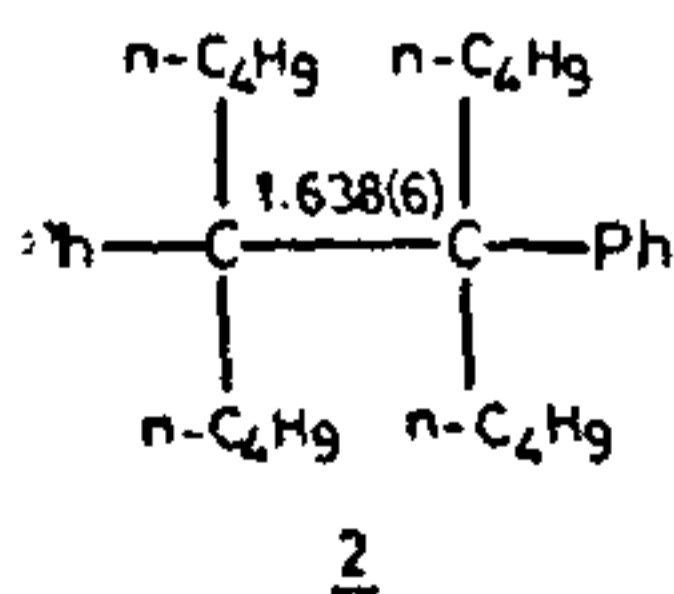
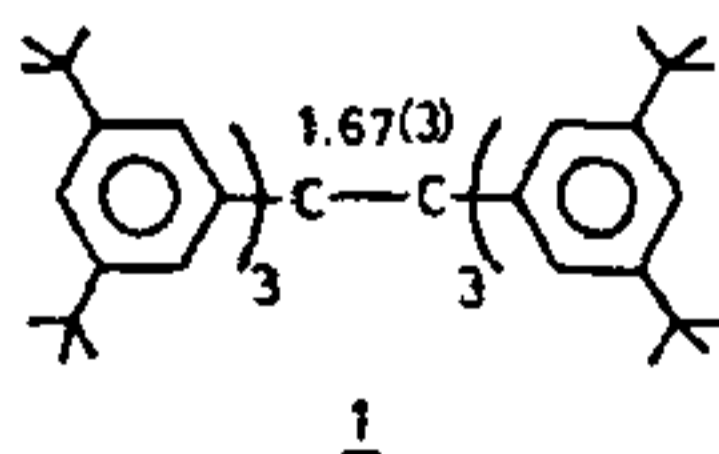
Organic structures with remarkable carbon-carbon distances

J. Chandrasekhar

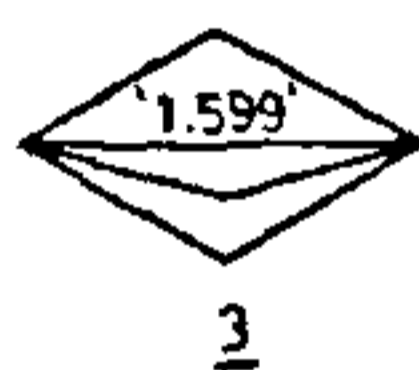
There is a general feeling amongst chemists that C-C bond lengths are entirely predictable and correspondingly uninteresting. Variations from average values ($C_{sp^3}-C_{sp^3}$: 1.530 (15) Å; C=C: 1.322 (14) Å; $C\equiv C$: 1.181 (14) Å, and 1.384 (13) Å in benzenoid rings)¹ are mainly due to steric repulsions involving substituents and not because of any novel electronic interaction. Nonbonded C-C contacts are even less of interest, as no non-covalent attractive force involving carbon atoms is expected, with the sole exception of π -stacking interactions.

The above generalizations hold good for a majority of systems. But a critical evaluation of known C-C distances shows a surprisingly large variation which deserves to be highlighted.

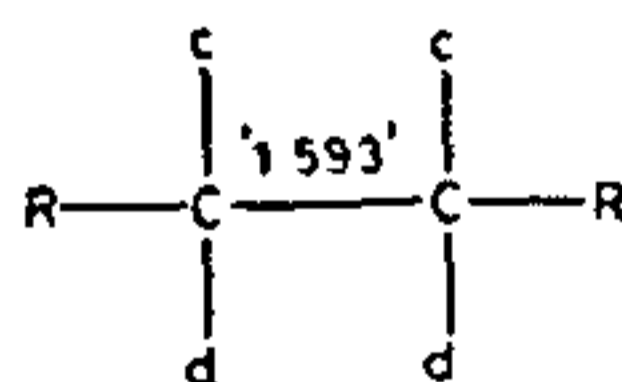
Let us begin with single bond lengths. Elongated bonds as found in 1 and 2



are easily attributed to steric interactions^{2,3}. Interestingly, the central C-C bond length in [1.1.1] propellane (3)

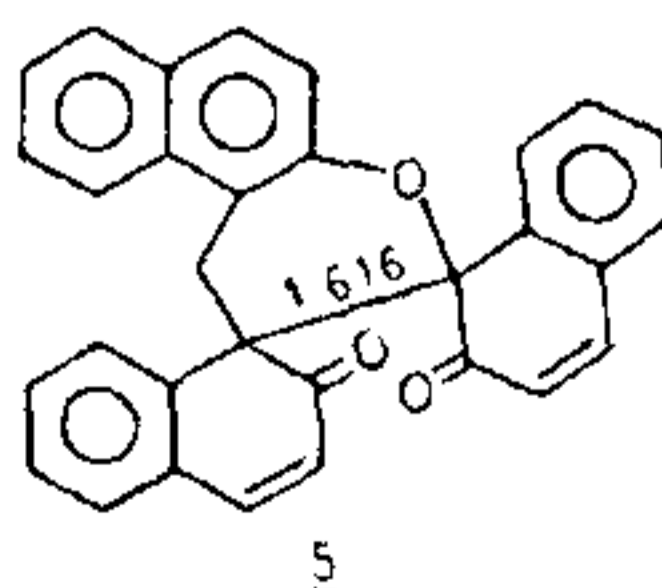


with two 'inverted' carbon atoms is not particularly long (average = 1.599 Å for the two distinct molecules present in the crystal)⁴. Similar values are observed as a consequence of captodative electronic interactions in 4 (ref. 4) although steric

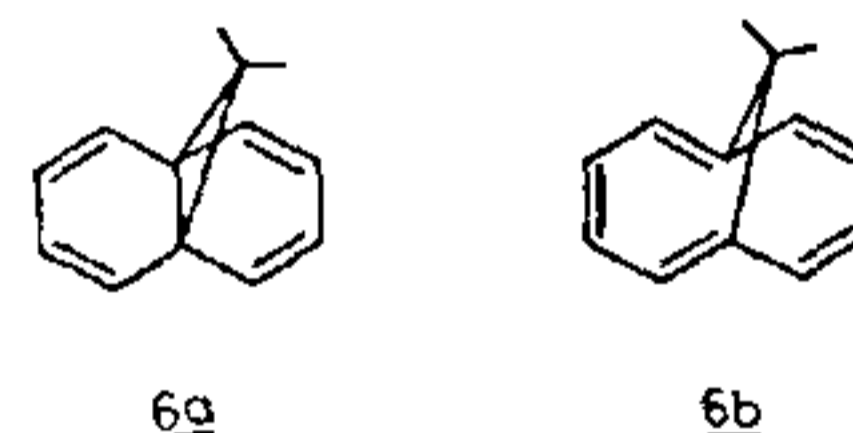


4 (c = CN, COOR, ---
d = SR, OR ---)

contributions are also present. The same effect is presumably responsible for the observed length as well as reactivity of a C-C bond in 5 (ref. 6).



Long C-C distances are also observed in conjugated molecules in which the σ bond can participate in a sigmatropic rearrangement. An exceptionally long bond of this kind has been determined in the 1,6-methano[10]annulene derivative, 6, which exists in the bisnorcaradiene (6a) and not the [10]annulene form (6b), on the basis of

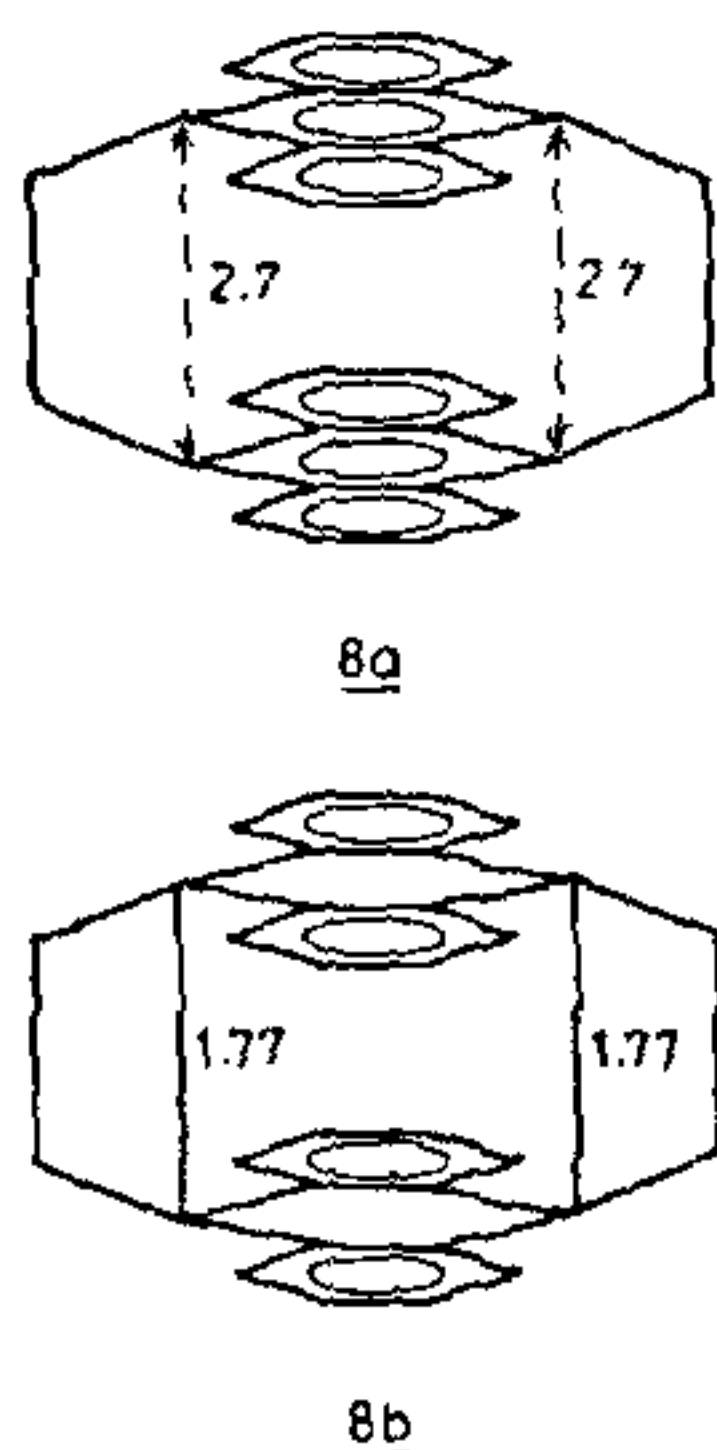


NMR results. The libration-corrected central bond lengths in the two distinct molecules present in the crystal are 1.836 and 1.780 (0.007) Å (ref. 7). *Ab initio* calculations had to be used to confirm the presence of the central C-C bond. It is interesting to speculate on the corresponding distance in the diphenylcarbene complex of buckminsterfullerene, 7, which is essentially 6 fused to a larger aromatic framework. NMR results



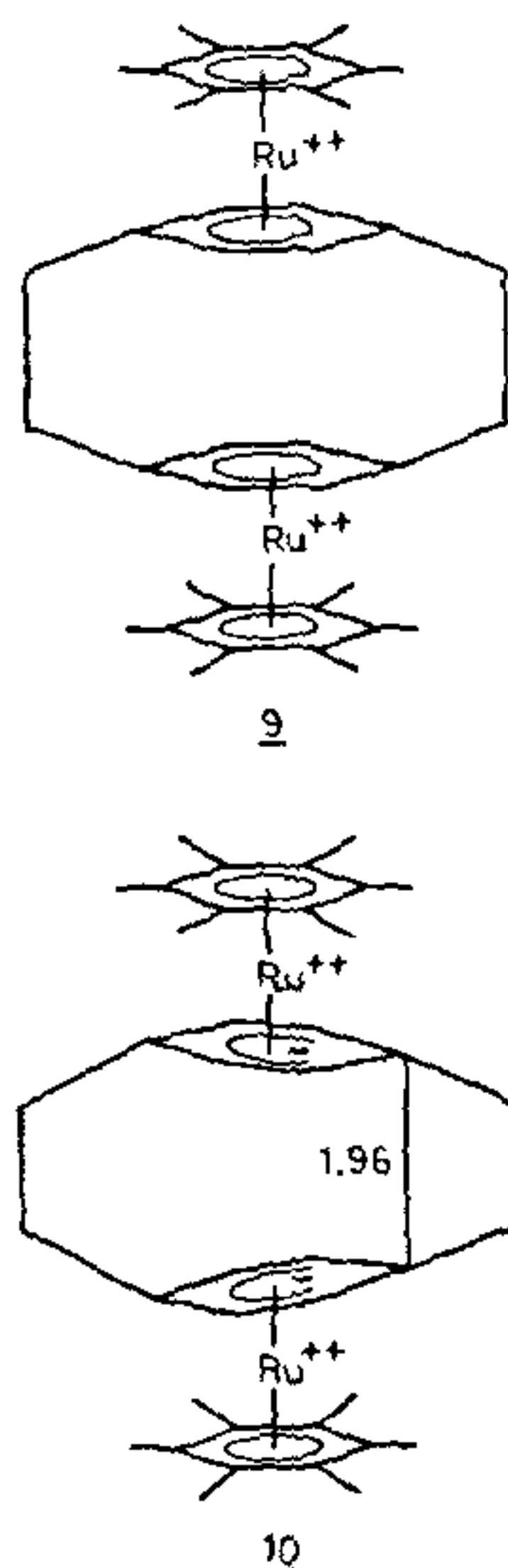
have been interpreted in favour of the [10]annulene form⁸.

Another class of compounds with long C-C bonds is obtained by introducing a σ bond between the rings of a cyclophane. For example, consider the curious case of bi-(anthracene-9, 10-dimethylene), **8**. It exists in two modifications (α and β) in the dark. X-ray structure of the β form (**8a**) reveals the presence of two anthracene moieties held apart by 2.7 Å (ref. 9). In the presence of light, a photo-isomer (**8b**) is



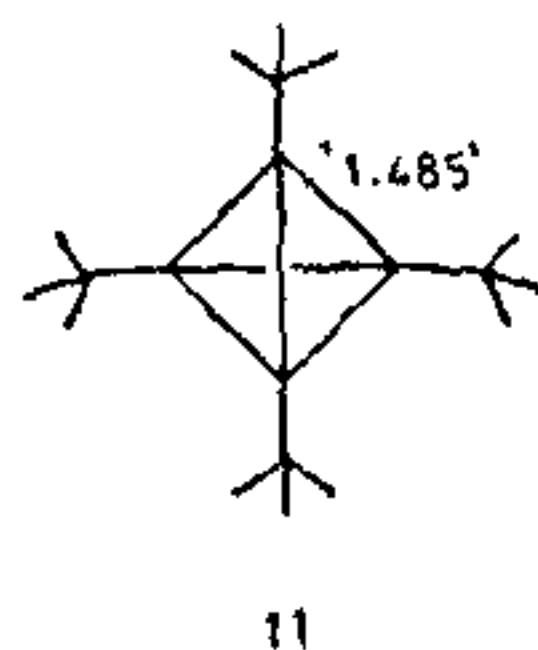
readily formed. It is expected to have two four-membered rings, on the basis of the usual photodimerization reaction of anthracene. The length of the newly formed symmetry-related C-C bonds in the two four-membered rings is remarkably high, 1.77 (1) Å (The corresponding distance in the dimer of anthracene is 1.61 Å.) To make matters even more exciting, the photo-isomer changes back into the β form in the dark. Can one view it as an unrecognized early example of bond-stretch isomerism?

Another spectacular example of a long C-C bond is derived from the diruthenium complex of a paracyclophane, **9**. Two-electron reduction leads to an unsymmetrical structure, **10**, in which two cyclohexadienyl anion decks are connected by a C-C bond. The corresponding length of 1.96 (3) Å is the longest C-C σ bond measured so far¹⁰. Of course, a careful electron count to satisfy the 18 electron rule for the metals atoms is needed to recognize the very existence of the C-C bond. This species and the isolobal variants of cyclophane ions should prove to be

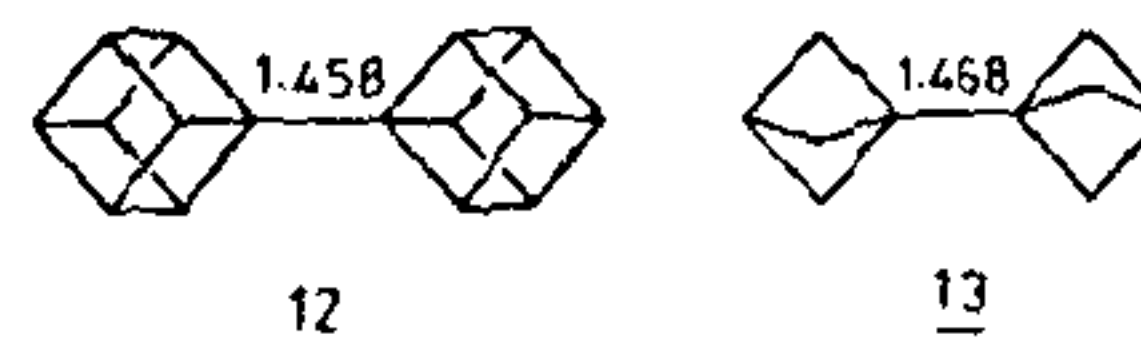


interesting systems for further study.

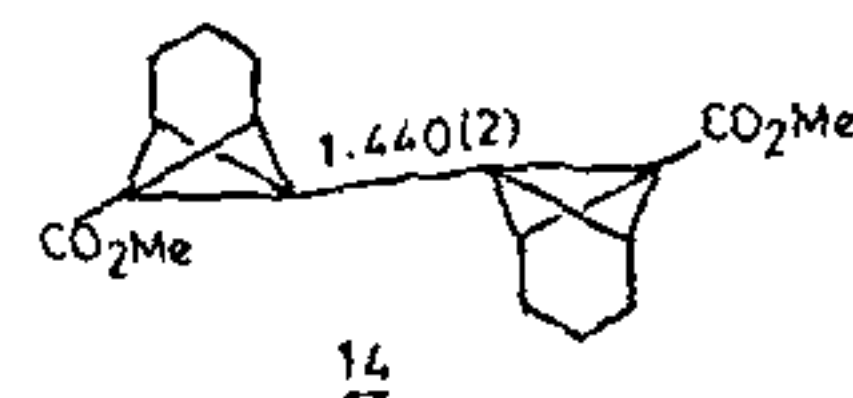
Molecules with the reverse type of distortion, viz. with exceptionally short C-C bond lengths, are also known. In small ring systems with bent bonds, atoms get close in order to maximize the overlap between the orbitals. In such cases, the interatomic distance is not a true reflection of the 'bond length'. An extreme example of this type is tetra-*tert*-butyltetrahedrane, **11** (average value of C-C distance in the cage: 1.485 Å)¹¹.



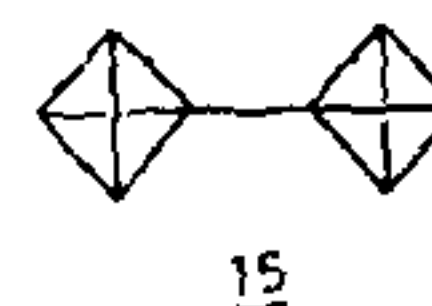
Genuine bond contractions can be achieved through rehybridization effects. Endocyclic bonds in small rings have high p character. Correspondingly, the exocyclic bonds have high s character and are relatively short. Inter-ring bonds in coupled ring systems, such as bicubyl (**12**)¹², [2]staffane (**13**)¹³, etc., are highly contracted. The value of 1.440 (2) Å found in a representative of



this series¹⁴, viz. the coupled bicyclo [1.1.0] butane derivative, **14**, is the



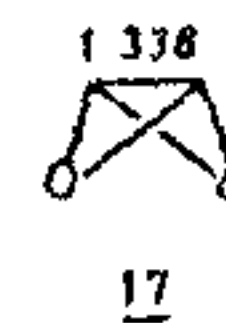
shortest non-cyclic (unbent) C-C single bond between saturated tetravalent carbon atoms observed so far. Theoretical calculations predict an even shorter bond length in bi-tetrahedryl, **15** (ref. 15).



Other modes of shortening C-C bond lengths are known. For example, the central C-C bond length in bicyclo [1.1.0]butane derivatives shows an interesting dependence on the flap angle between the three-membered rings¹⁶. With additional contributing factors due to substituents, the central C-C distance in the ketone, **16**, corresponds

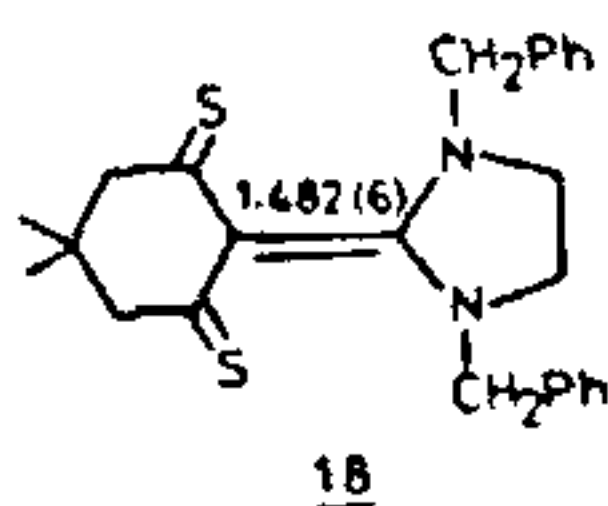


to the shortest formal single bond length measured so far, 1.408 (3) Å (ref. 16). Theoretical calculations suggest additional means of reducing the central bond length in the bicyclobutane skeleton, viz. through heteroatom perturbation. Thus, the diepoxide of acetylene, **17**, is predicted¹⁵ to be essentially a π complex with a C-C single bond length of 1.34 Å!

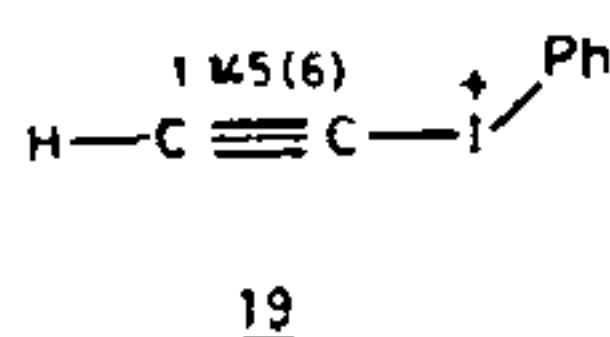


Lengths of C-C double and triple bonds are also susceptible to geometric distortions and electronic effects. Invariably, these perturbations lead to

significant increase in bond lengths. In the highly twisted push-pull ethylene, **18**, the inter-ring C=C distance is 1.482 (6) Å (ref. 17), almost the value for a single bond between two sp² carbon atoms¹.

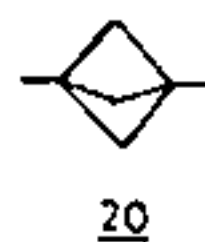


Bond contractions in multiply bonded systems through rehybridization are not expected to be very large. The C-C force constant is too large to permit distortions without changing the bond order. Nevertheless, the triflate salt of the cation **19** springs a surprise by



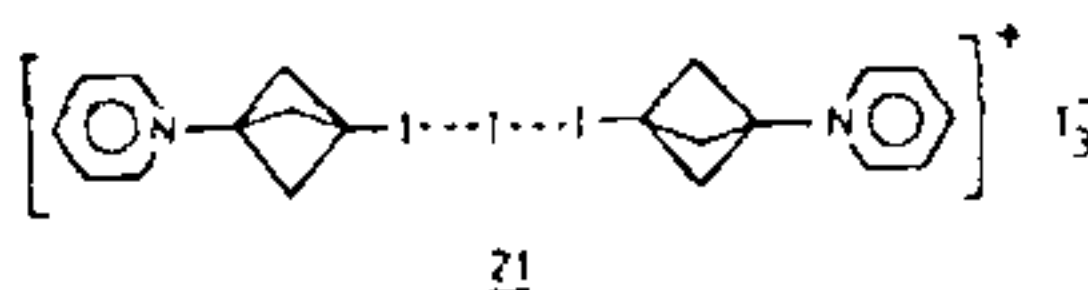
sporting a C-C bond length of 1.145 Å (ref. 18). It is the shortest C-C distance ever measured. The synthetic utility of this compound is being actively explored, but not the electronic origin of the exceptionally short C-C bond length.

Non-bonded contacts between carbon atoms can be induced through π -stacking forces. But drastically short distances can be achieved by 'brute force', viz. by constructing rigid skeletons, such as cyclobutane, cubane, etc. The limit seemed to have been achieved in the bicyclo [1.1.1] pentane cage (**20**),



with a non-bonded distance of 1.89 Å (ref. 19). However, it has been pointed out that the 1,3-distance in this system is sensitive to bridgehead substituents. Electron-withdrawing groups tend to decrease the non-bonded contact²⁰. Following this lead, a structure with the shortest C-C nonbonding distance has recently been described²¹. The compound is a quaternary pyridinium salt of bicyclo-[1.1.1]pentane with an iodine at the other bridgehead position. Two

such units are linked together by a central iodide ion. An additional I⁻ counterion restores charge neutrality. The two equivalent 1,3-'nonbonding' distances in this structure (**21**) are 1.80



(2) Å. The problem now is to prove that there is no bonding between the bridgehead carbon atoms. The authors point out potential propellane-like canonical structures with a central C-C bond. A related example which comes to mind is the calculated 1,3-distance of less than 1.60 Å in the 1-bicyclo[1.1.1]pentyl-cation (**22**). Detailed analysis revealed that significant bonding interaction exists between the bridgehead atoms in this unusual cation²².



The existing records for unusual bond lengths in organic molecules are unlikely to survive for long, given the constantly developing capabilities of synthetic chemists and the increasing insights provided by theory. Structural chemists will continue to have a lot of work on their hands.

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- Dedication* The article is dedicated to Professor K. Venkatesan on his formal retirement from the Department of Organic Chemistry, Indian Institute of Science, Bangalore.
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