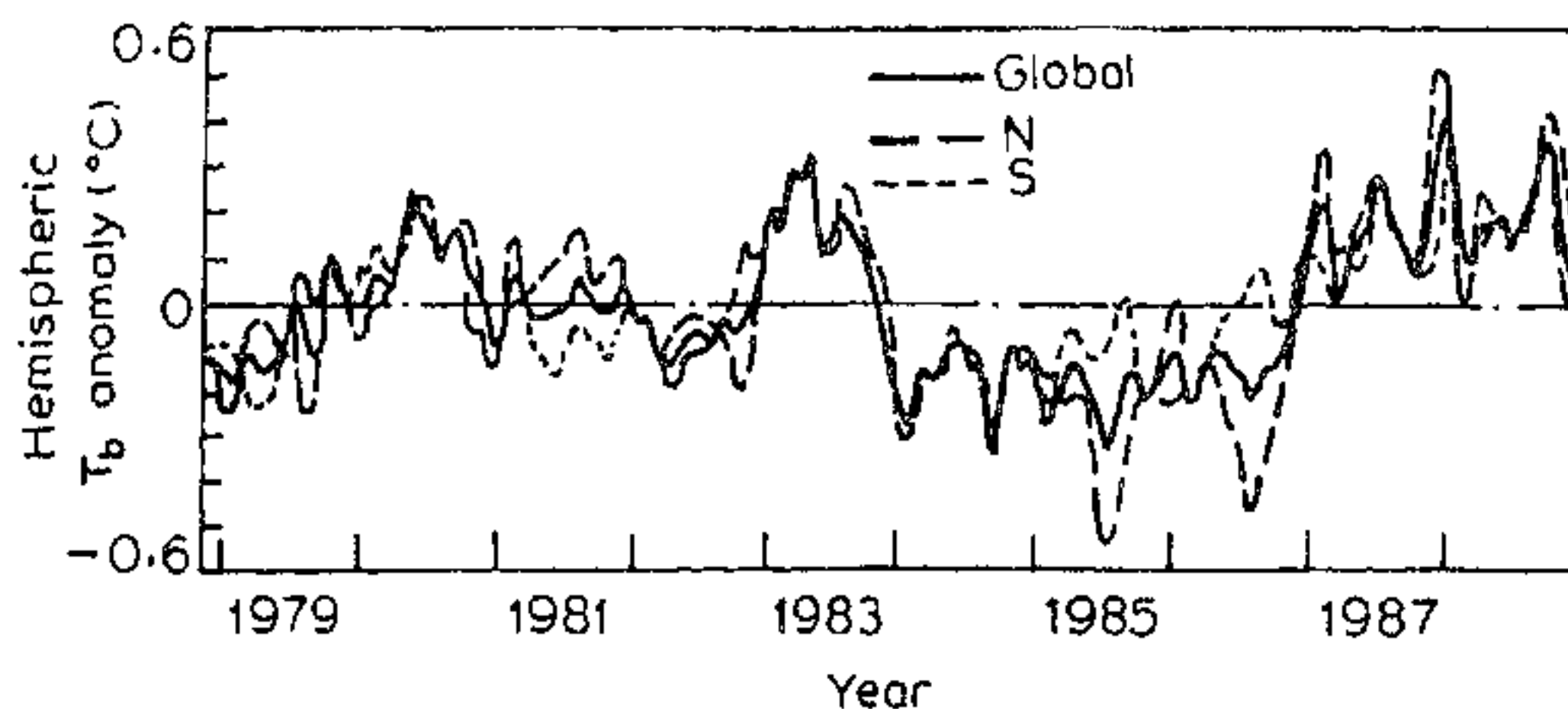


lies from thermometers and the MSU's monthly mid-tropospheric temperature anomalies to be similar, with a correlation coefficient of 0.89, but the surface anomalies were typically two to three times as great as the MSU anomalies and were probably caused by daytime solar heating and night-time cooling of the surface. Considering therefore the important issue of whether near-surface temperatures or deep-layer temperatures should be monitored for detection of climate change, they suggest that it would be best to monitor both in order to gain an understanding of how the entire troposphere behaves, the latter having, however, the advantage of freedom from surface effects and being capable therefore of providing an earlier signal of possible greenhouse warming.

Large fluctuations in the hemispheric and global temperatures were observed during the 10-year period 1979–1988 (see figure), the warmest years, in decreasing order, being 1987, 1988, 1983 and 1980, and the years 1984, 1985 and 1986 being the coolest. No obvious long-term trend was noticed, anomalies during the first five years nearly balanc-



Hemispheric temperature anomalies for the 10-year period 1979 through 1988. S and N refer to southern and northern hemispheres respectively; the global time series is in a continuous line.

ing those during the last five years. The 1988 and 1980 warm events were traced to the mid-latitudes, while the 1987 and 1983 warm events were associated with El Niño/Southern Oscillation events (ENSOs), the 1983 event causing globally averaged temperatures to rise more in several months than what would be expected in several decades with enhanced greenhouse warming. The period 1984 to 1986 was dominated by cooler-than-normal tropical air. There were nine cool or warm years and only one year

(1981) that could be considered 'average' in the 10-year period studied. This makes one, as it does the authors, wonder what 'normal' for global temperatures means, since 'normal' can mean either warm or cool conditions.

1. Spencer, R. W. and Christy, J. R., *Science*, 1990, **247**, 1558.

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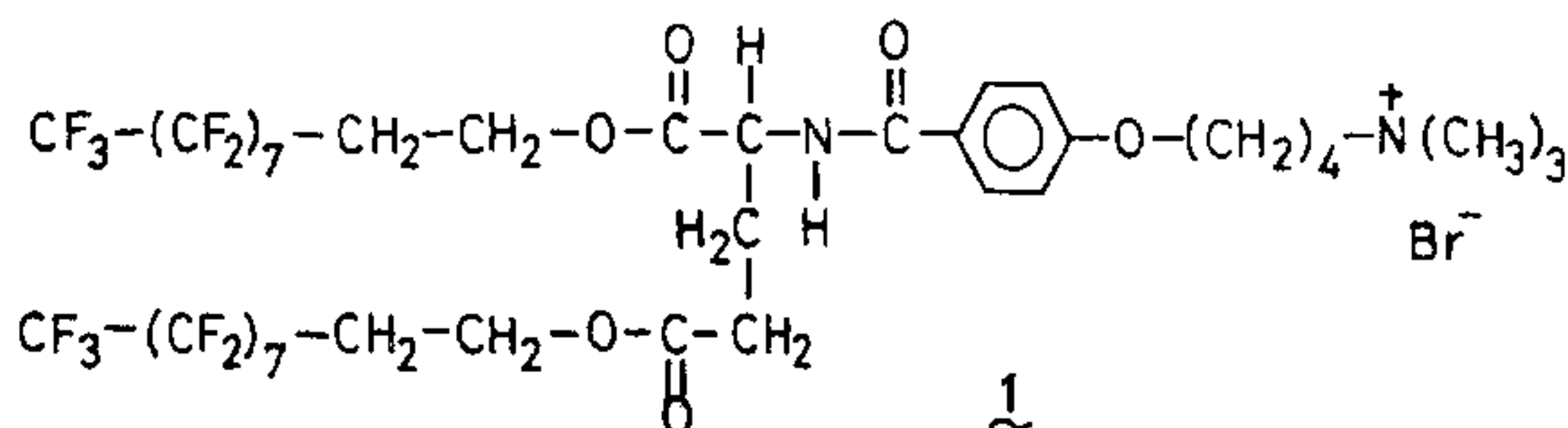
Solvophobic effects drive self-assembly and neutral molecule recognition in organic media

P. Balaram

Water and the hydrophobic effect¹ are central to biological organization. Membranes and the convoluted structures of globular proteins are two striking examples of the importance of hydrophobic interactions in facilitating molecular self-assembly and the three dimensional folding of complex macromolecules. Hydrophobic effects, or the tendency of apolar groups to cluster together and avoid exposure to the aqueous medium, are often crucial in biological recognition processes like ligand-receptor interactions. Can self-organization and specific recognition between neutral molecules be achieved in non-aqueous media? The thrust of several recent reports in this area suggests that Nature's devices can be mimicked, in albeit limited fashion, in organic solvents.

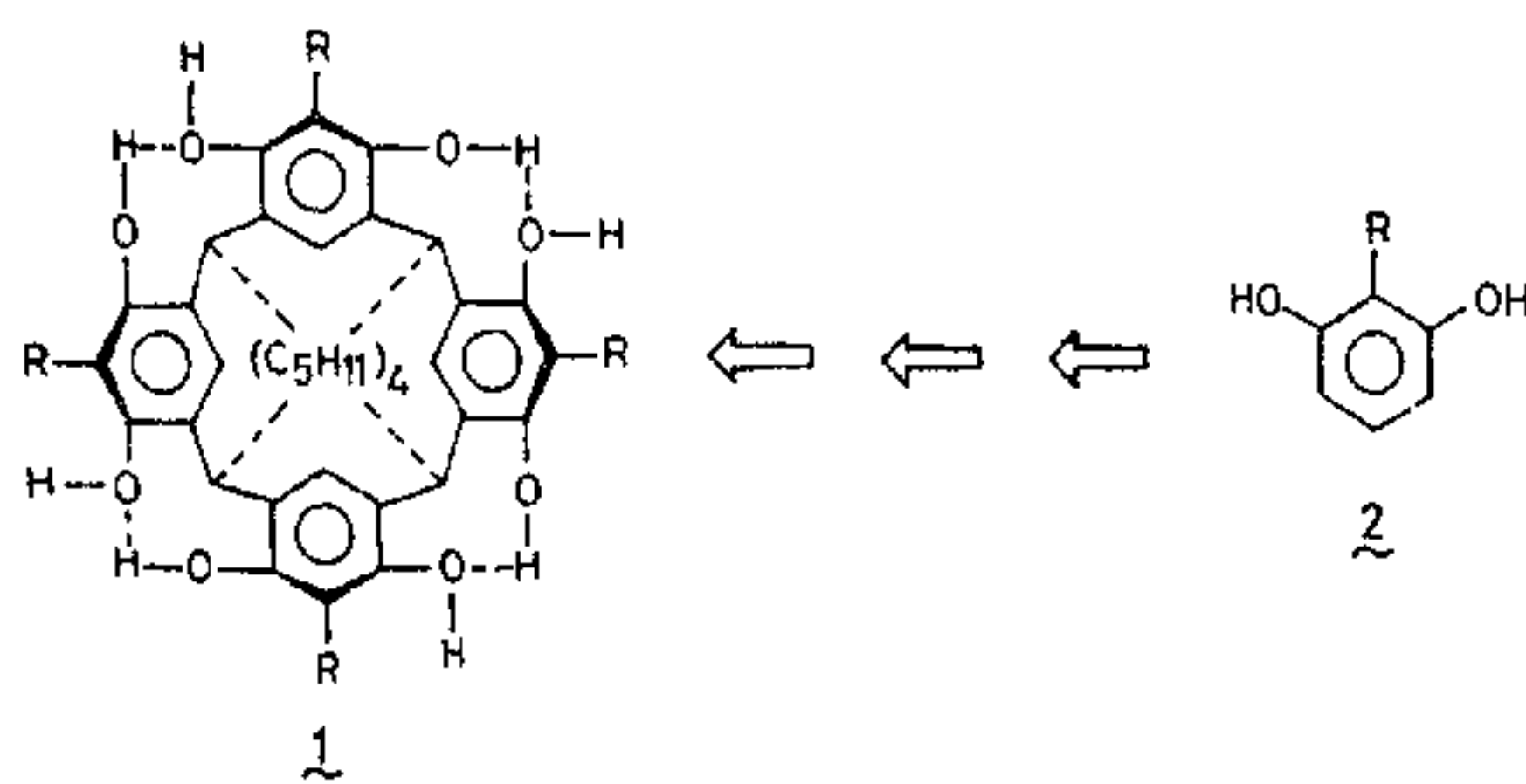
An exciting report, from Japan by Ishikawa *et al.* at Kyushu University, describes the spontaneous formation of bilayers by perfluoroalkyl derivatives, in organic media². Compound 1 is amphiphilic and forms bilayers in water³. Modification of the structure to replace the polar head by a neutral apolar group yields 2, which forms highly organized aggregates in cyclohexane. This feature is evident from the high intensity of the circular dichroism bands

due to the aromatic rings (2 is chiral and is derived from L-glutamate). Electron microscopy of samples stained with Pb(II)bis(acetylacetonate) revealed the presence of vesicles of diameter 200–1000 Å. Alternative morphologies like twisted tapes are also observed as a function of temperature. The authors interpret their electron micrographs and CD data in terms of formation of a bilayer structure (Figure 1). The fluorocarbon chain by virtue of its limited



Cram's cavitands, Limaye and *Rasayanam*

Among the many intricate molecular receptors synthesized by Donald Cram (Nobel Prize in Chemistry, 1987) are the structures highlighted in the accompanying article. An important intermediate in the construction of such molecules is the structure 1, which in turn is derived from the simple starting material, 2-alkyl resorcinols, 2. Substitution of resorcinol at the 2-position was first developed in Pune, by Dattatraya Balkrishna Limaye (1887–1971) in the 1930s. Cram's 1990 paper¹ quite appropriately cites the procedure published by Limaye and Ghate in *Rasayanam*².



Limaye's interest in chemistry was evident even while a student at Fergusson College, Pune, when he started a venture to produce fine chemicals—the Balkrishna Rasashala³. The major part of his career was spent at the Ranade Institute of Industrial Chemistry (1912–1946), an institution originally established by Gopal Krishna Gokhale. Here Limaye rose from industrial chemist to director and established a flourishing centre for applied organic chemistry. It was here that he developed his 'Nidhone Process' for the synthesis of 2-substituted resorcinols and furocoumarins, both of which are early landmarks in the development of Indian organic chemistry. Limaye's devotion to chemistry

and the Indian ethos led to his starting the journal *Rasayanam* in 1936, where he published several original and important findings. He had a dominant role in shaping the development of a viable school of organic chemistry in Pune, culminating in the present chemistry department at the Poona University campus at Ganeshkhind. Appropriately, the department celebrated the Limaye centenary in 1987, with a symposium devoted to trends in contemporary organic chemistry.

Cram's citation, of an over half a century old paper from *Rasayanam*,

1. Bryant, J. A., Knobler, C. B. and Cram, D. J., *J. Am. Chem. Soc.*, 1990, 112, 1254.
2. Limaye, D. B. and Ghate, I., *Rasayanam*, 1936, 1, 39.
3. Biographical information on D. B. Limaye has been taken from a write-up by Dr K. G. Marathe, kindly provided by Prof. N. S. Narasimhan.

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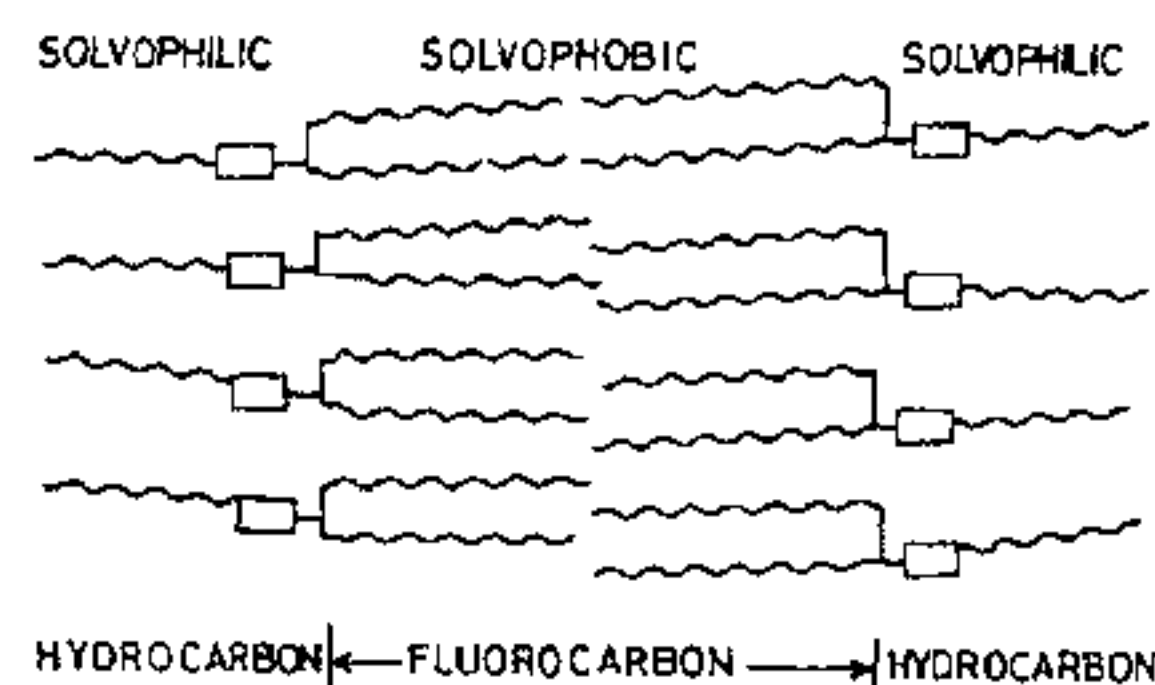
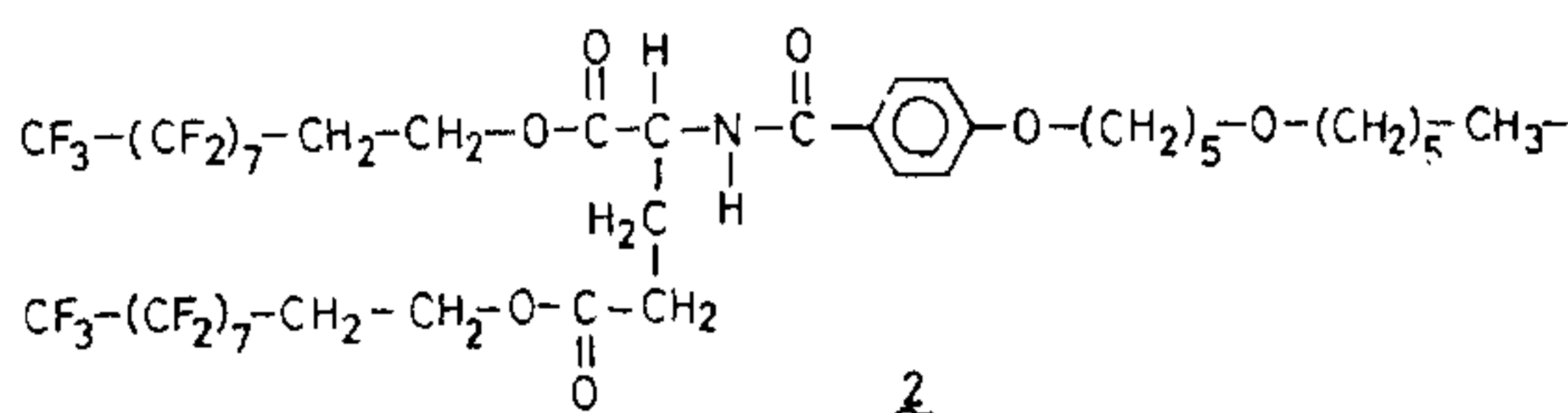
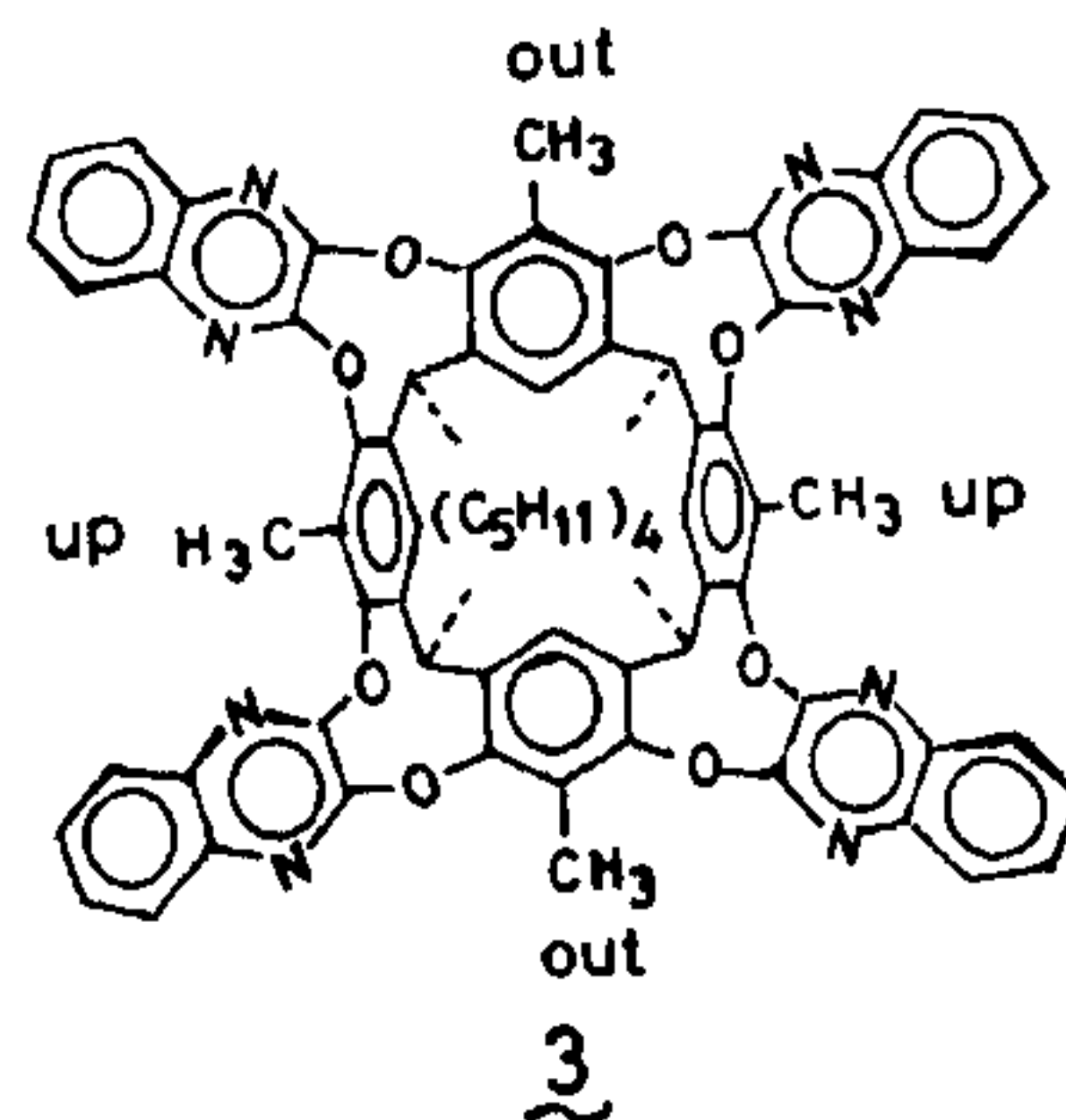


Figure 1.

miscibility with the hydrocarbon solvent acts as the 'solvophobic unit'. Ishikawa *et al.*² are also quick to point out that 'compartmentalization of the molecular space can be realized even in organic media' and optimistically anticipate 'emergence of a wholly new branch of organic chemistry'.

In a different vein Donald Cram and coworkers at the University of California at Los Angeles, report on a high degree of structural recognition achieved by neutral molecules, with large apolar surfaces, in chloroform solution⁴. Importantly, this molecular recognition process occurs in the absence of any obvious electrostatic or hydrogen bonding interaction. Structure 3 (the latest in a long series of 'molecular vessels' from Nobelist Cram), forms extraordinarily stable dimers in chloroform ($K_d \sim 87,000 \text{ M}^{-1}$, $\Delta G^\circ \sim -6.6 \text{ kcal mol}^{-1}$ at 12°C)⁵. Dimerization is visualized as in Figure 2, with the two molecules being twisted by 90° , permitting methyl projections on one to nestle into host cavities in the partner. Replacement of the projecting methyl groups by ethyl abolishes dimerization. A crystal structure of 3 reveals as many as 70 atom-atom van der Waals contacts at the interface, with a further 44 atoms at a contact distance plus $0.1\text{--}0.2 \text{ \AA}$ (ref. 4). Such



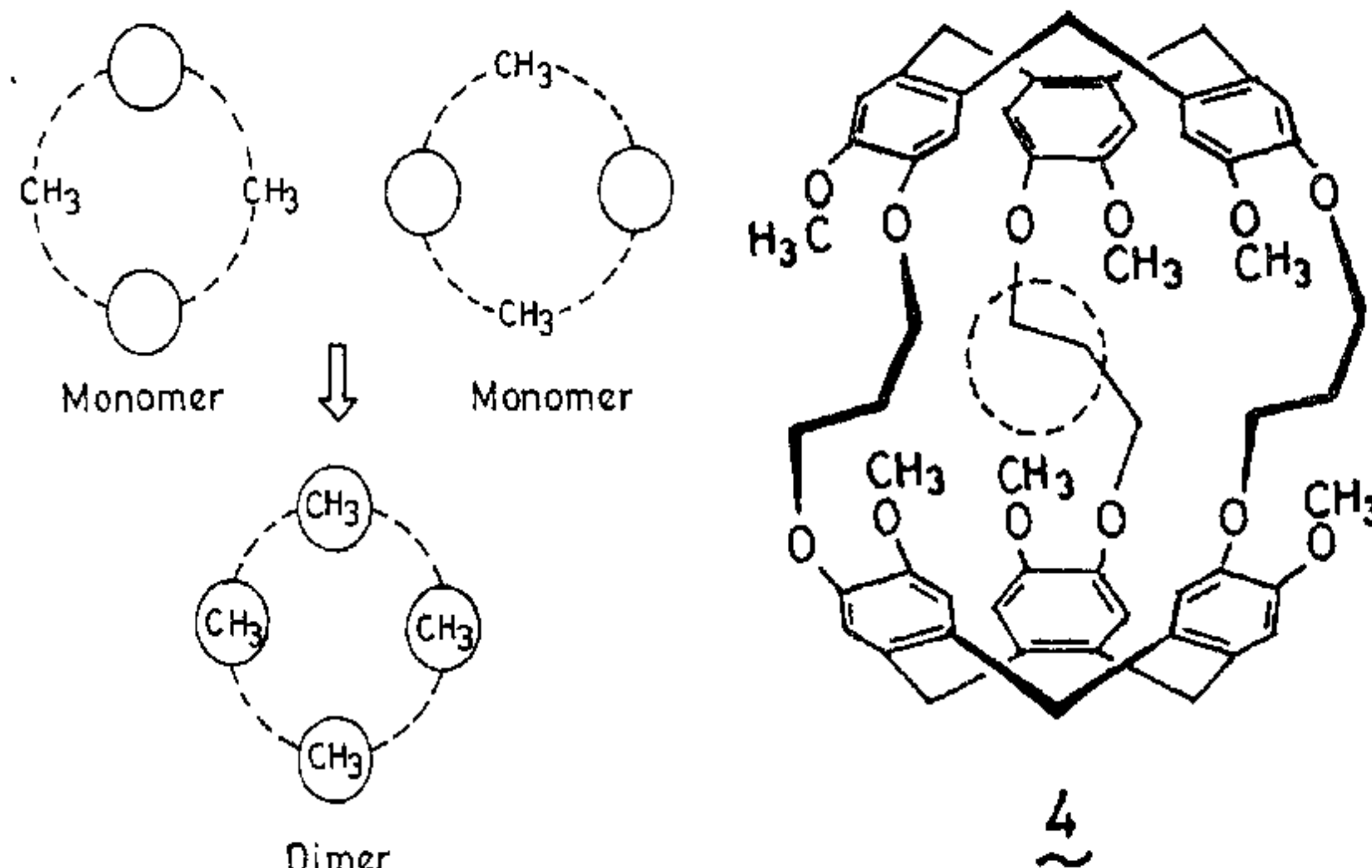


Figure 2.

interactions between large pre-organized apolar surfaces in organic solvents are probably facilitated by entropic advantages of desolvation⁵. A recent crystal structure determination of

a guest chloroform molecule (circle) entrapped in a molecular host 4, provides a further example of complexation in the absence of hydrophobic effects⁶. While several such instances are known, Canceill *et al.*⁶ suggest that

these be viewed as van der Waals molecules, thus extending the definition to species with appreciable lifetimes.

Non-aqueous media should be a happy hunting ground for organic chemists bent on imitating Nature, especially for those who have a phobia about working in water.

1. Tanford, C., *The Hydrophobic Effect*, 2nd edn. Wiley, New York, 1980.
2. Ishikawa, Y., Kuwahara, H. and Kunitake, T., *J. Am. Chem. Soc.*, 1989, **111**, 8350.
3. Kunitake, T., Tawaki, S. and Nakashima, N., *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3235.
4. Bryant, J. A., Knobler, C. B. and Cram, D. J., *J. Am. Chem. Soc.*, 1990, **112**, 1254.
5. Bryant, J. A., Ericson, J. L. and Cram, D. J., *J. Am. Chem. Soc.*, 1990, **112**, 1255.
6. Canceill, J., *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 1246.

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