

The Structures of Three Naphthalene Tetrachlorides

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OF the six possible geometric isomers of naphthalene 1,2,3,4-tetrachloride, several are known, but only one has been assigned a structure unambiguously. This is the α -isomer, m.p. 182°, which has the configuration indicated diagrammatically at (I), and the conformation in the solid state indicated at (II).¹

The γ -isomer, m.p. 134°, has been assigned by Schütz and Hahnfeld² to one of the structures (III) and (IV) on the basis of its rate of alkaline dehydrochlorination. We have now examined its proton magnetic resonance spectrum. This shows that the environments of H₁ and H₄ (and likewise of H₂ and H₃) are the same (an A₂X₂ spectrum). Only four of the six possible naphthalene tetrachlorides should have this symmetry, and the coupling constants for the pairs of aliphatic protons provide further information. All three are large ($J_{1,2} = J_{3,4} = J_{2,3} = 8.0$). Karplus' relationship³ tells us that there must be a large* angle between each pair.† The only possible conformation, then, is that having all four hydrogens axial or pseudo-axial, and hence all four chlorines equatorial or pseudo-equatorial.

Structure (III) is therefore correct, and (V) is the predominant conformation in solution.

Schütz and Hahnfeld² assigned to the δ -isomer, m.p. 96°, one or other of the structures (VI) and (VII). Proton magnetic resonance spectroscopy again allows a decision between these two possibilities. This isomer has a very unsymmetrical ABCD spectrum (with $J_{AC} = J_{BD} = J_{AD} = 0$), as is consistent with either (VI) or (VII), but with no other configuration. The coupling constant between the 2- and 3-hydrogen atoms, $J_{2,3}$, is very large (10.9). These two hydrogen atoms must therefore both be axial; (VI) must be the structure, and (VIII) the preferred conformation in solution. The coupling constants $J_{1,2}$ and $J_{3,4}$ are consistent with this structure.

From reaction of naphthalene with chlorine in carbon tetrachloride in the sunlight, a new naphthalene tetrachloride, which we designate the ϵ -isomer, is formed, together with the more insoluble γ -isomer. We have isolated the new compound by fractional crystallisation of the mixed tetrachlorides; it has m.p. 85–87°. Its p.m.r. spectrum shows that, like the α - and

* The possibility of a very small angle between the C–H bonds can be excluded by examination of models.

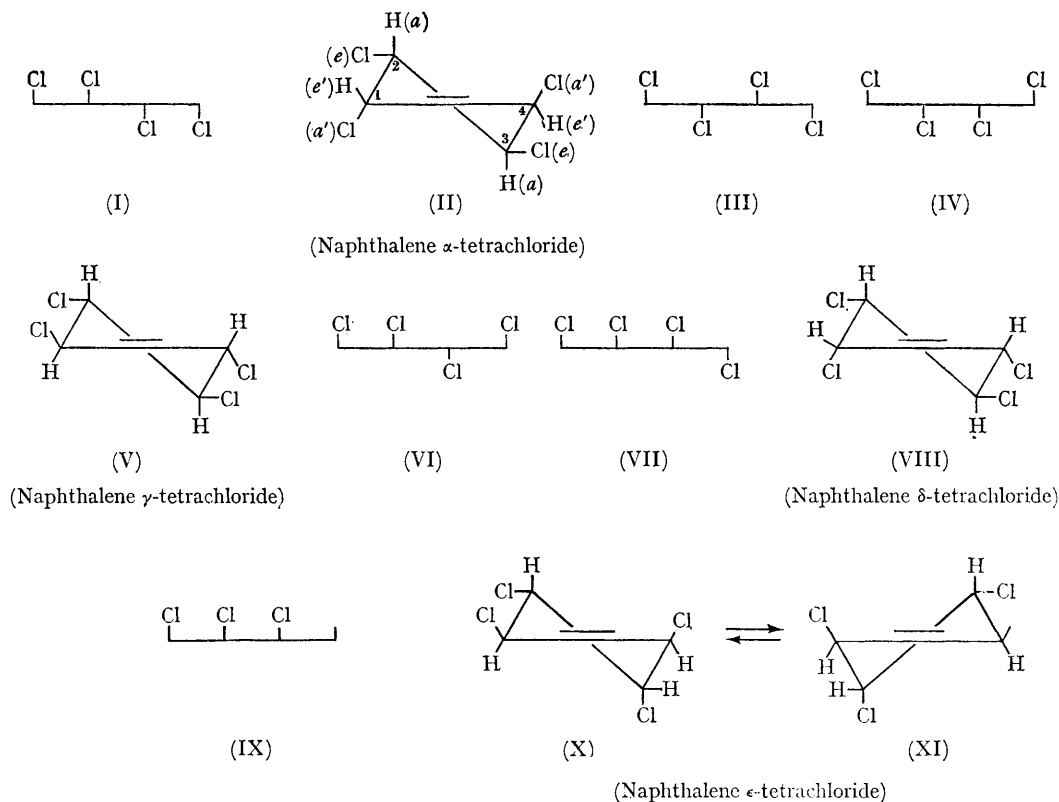
† We assume, following other writers,⁴ that the relatively unstrained "pseudo-chair" form of the cyclohexene-like system, exemplified for the α -isomer in (II), is favoured in compounds of this type.

¹ M. A. Lasheen, *Acta Cryst.*, 1952, 5, 593.

² F. Schütz and K. Hahnfeld, *Chem. Ber.*, 1952, 85, 131.

³ M. Karplus, *J. Chem. Phys.*, 1959, 30, 11.

⁴ cf. W. G. Dauben and K. S. Pitzer, "Conformational Analysis", in "Steric Effects in Organic Chemistry", ed. M. S. Newman, Wiley, N.Y., 1956.



TABLE

Proton magnetic resonance spectra of naphthalene 1,2,3,4-tetrachlorides

Compound	α -Tetrachloride	γ -Tetrachloride	δ -Tetrachloride	ϵ -Tetrachloride
M.p.	182°	134°	96°	85—87°
Spectrum type:	A_2X_2	A_2X_2	ABCD	A_2X_2
τ -Values (p.p.m.):				
Aromatic:	2.48 (single)	2.26 (single)	2.2—2.7 (unsymm.)	2.4 (A_2X_2)
1-H	4.28	4.48	4.56	4.53
2-H	4.93	5.42	5.53	4.96
3-H	4.93	5.42	5.08	4.96
4-H	4.28	4.48	4.60	4.53
Coupling constants (c./sec.):				
$J_{1,2}$	3.5 \pm 0.4	8.0 \pm 0.4	3.2 \pm 0.4	5.8 \pm 0.4
$J_{2,3}$	11.0 \pm 0.6*	8.0 \pm 0.6	10.9 \pm 0.4	\geq 3.5
$J_{3,4}$	3.5 \pm 0.4	8.0 \pm 0.4	7.6 \pm 0.4	5.8 \pm 0.4
Chlorine positions in solution	$a'eea'$ *	$e'eee'$	$a'eee'$	$a'ae'e' \rightleftharpoons e'ea'a'$

* Tetrahydrofuran or dioxan as solvent; we have not been able to determine $J_{2,3}$ for this compound in deuteriochloroform, because of its low solubility and the resulting very low intensity of the relevant outer peaks of the A_2X_2 spectrum.

γ -isomers, the environments of H_1 and H_4 (and likewise of H_2 and H_3), are magnetically equivalent. Of the two remaining possibilities having this symmetry, *viz.* (IV) and (IX), the latter should, in either of its possible conformations, have low coupling constants for each pair of protons. This does not accord with the experimental data (see Table). The former, on the other hand, should be an equilibrium mixture containing the enantiomorphic conformations (X) and (XI) in equal amounts. Each of these should have a large coupling constant (note the large angle between the C_1H and C_2H bonds in (X) for one of the outer pairs of protons and a small coupling constant for the other. The rapidly equilibrating mixture should have coupling constants, $J_{1,2}$ and $J_{3,4}$, equal and intermediate between a high value of about 8 or greater and a low value of about 3. The observed value, 5.8, is consistent with this and only this structure.

⁵ P. B. D. de la Mare, R. Koenigsberger, J. S. Lomas, V. Sanchez del Olmo, and A. Sexton, *Rec. Trav. chim.*, 1965, **84**, 109.

The other naphthalene tetrachlorides were prepared essentially as is described in the literature; (*cf.* reference 2). In isolating the δ -isomer, chromatography on silica gel proved helpful. The melting points agreed satisfactorily with those recorded by other workers; satisfactory analyses were obtained for all the isomers, which had characteristic infrared spectra. Their p.m.r. spectra (determined on a Perkin-Elmer 60 Mc./sec. spectrometer, in deuteriochloroform, with tetramethylsilane as reference, except where otherwise noted) did not show the presence of any isomeric material. The Table shows the τ -values and coupling constants. The results will be discussed in more detail elsewhere, as will be the mechanistic implications of the modes of formation of these compounds.⁵

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