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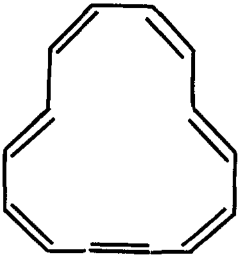
THE STRUCTURES OF THE TWO ISOMERS OF MONODEHYDRO[14]ANNULENE

TERRY M. CRESP* and FRANZ SONDHEIMER[1]
Chemistry Department, University College London,
20 Gordon Street, London WC1H 0AJ, England.

Abstract: *Variable temperature ^1H nmr spectrometry has shown that the "unstable" isomer of monodehydro[14]annulene possesses the symmetrical di-trans configuration 1 or 2, and the "stable" isomer (the precursor of [14]annulene) possesses the tri-trans configuration 4.*

Some years ago it was shown that the oxidative coupling of *trans,trans*-tetradeca-4,10-diene-1,7,13-triyne[2] with cupric acetate in pyridine and subsequent rearrangement with potassium *tert*-butoxide leads, *inter alia*, to two isomers of monodehydro[14]annulene (cyclotetradeca-1,3,5,7,9,11-hexaen-13-yne).[3] One of these [the "unstable" isomer; mp 95-100° dec.; main λ_{max} (isooctane) 314 nm (ε 95,500)] was readily converted to the other [the "stable isomer; mp 153-154°; main λ_{max} (isooctane) 311 nm (ε 85,000)] by allowing a dilute ether solution to stand without protection from daylight, or, more rapidly, by irradiation of a refluxing benzene solution with a 100 Watt lamp.[4]

As expected of conjugated systems containing 14 out-of-plane π-electrons, the ^1H nmr spectrum of each isomer showed it to be diatropic, the outer protons resonating at low field (*ca.* δ 8.5-7.3) and the inner ones at very high field (*ca.* δ-0.7).[3,5] The ratio of these two sets of bands in each compound was found to be *ca.* 5:1, indicating the existence of ten outer and two inner protons. It followed that each monodehydroannulene was made up of four *cis* and two *trans* double bonds. The conformers 1 and 2 were considered most likely for these compounds [3,5]



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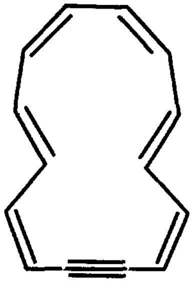

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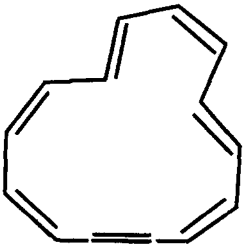

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Subsequent studies with related compounds made it very doubtful that such conformational isomers could be isolated as discrete entities at room temperature, and it was considered most likely that the two monodehydro[14]annulenes differ in the sequence of the *cis* and *trans* double bonds; *e.g.* they might be represented by structures 1 or 2 for one isomer, and structure 3 for the other. Unfortunately, X-ray crystallographic studies carried out over a number of years by different groups of workers on each isomer as well as on the beautifully crystalline 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone complexes, provided no answer to this problem.

We now report that a reinvestigation of the ^{1}H nmr spectra of each isomer at different temperatures has finally resolved this structural problem. The ^{1}H nmr spectrum of the "unstable" isomer (Figure 1) is essentially temperature independent in the range -80° to 27°. *In particular, there is no change in the high field coincident double doublet and this* isomer therefore possesses the symmetrical structure 1 or 2 as previously suggested.[5]

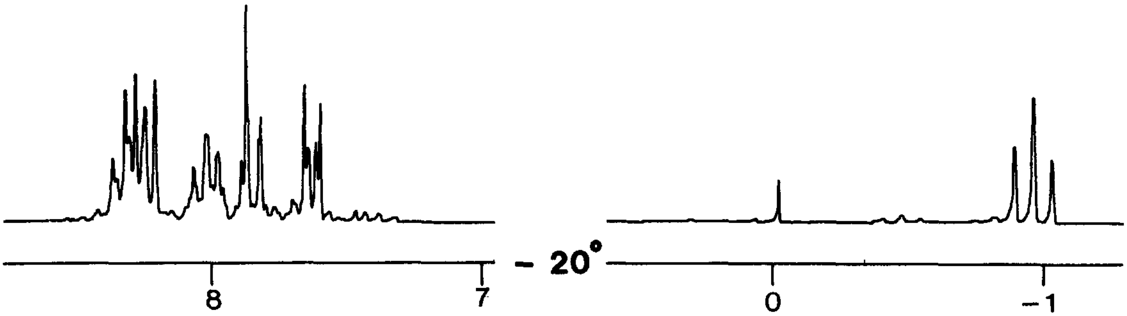
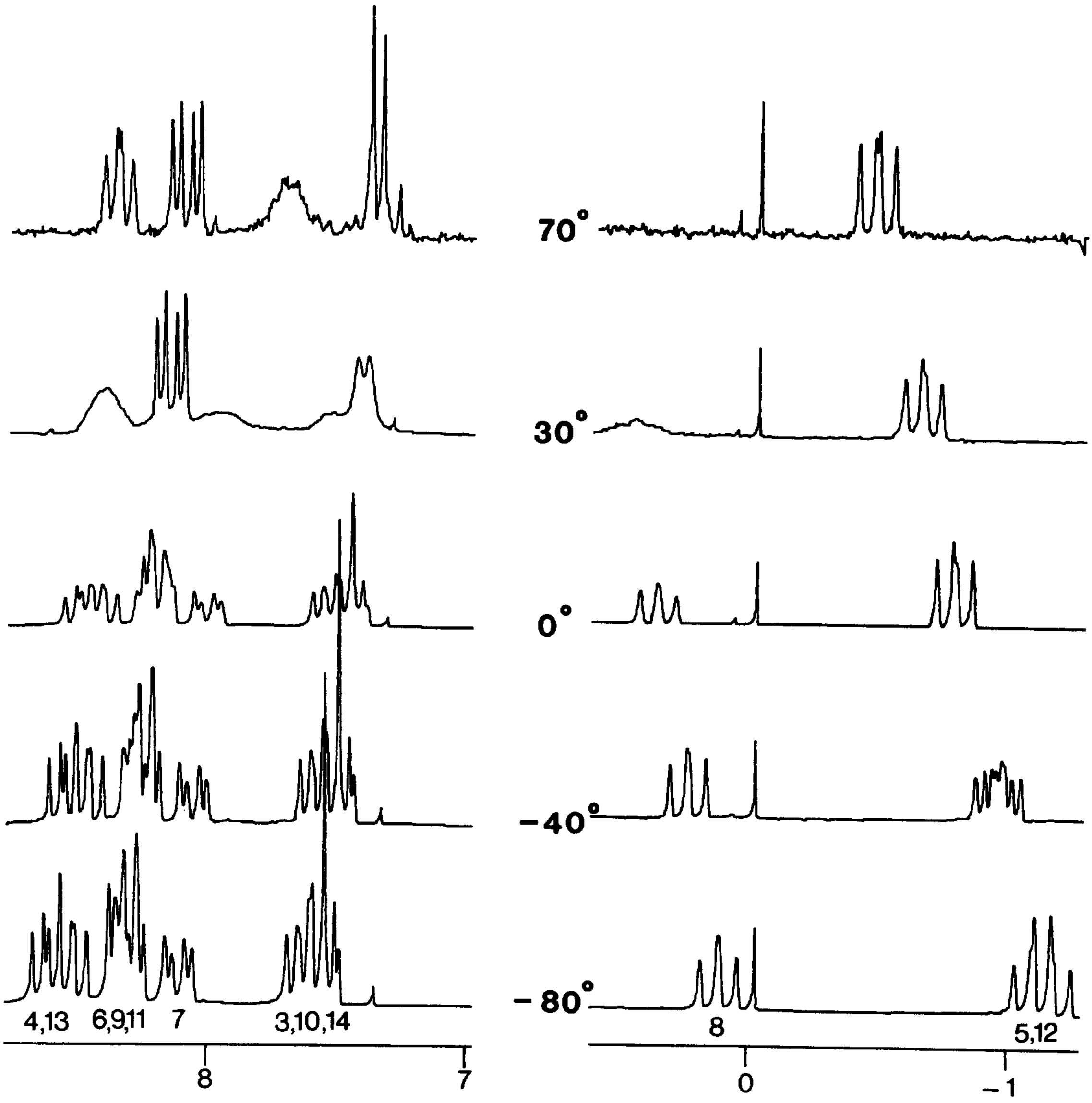


Figure 1. ^{1}H nmr spectrum of "unstable" isomer 1 or 2 (CD_2Cl_2,200 MHz) at -20°.

The ^{1}H nmr spectrum of the "stable" isomer, by contrast, shows a dramatic temperature dependence (see Figure 2). Analysis of the spectra was assisted by homonuclear decoupling experiments. ^{1}H nmr (δ,CD_2Cl_2,-40°) 8.63 (1H, dd, $J_{4,3}$8.8 Hz, $J_{4,5}$12.4 Hz, H-4), 8.54 (1H, dd, $J_{13,14}$8.8 Hz, $J_{13,12}$12.0 Hz, H-13), 8.2–8.4 (3H, m, H-6, H-9, H-11), 8.13 (1H, dd, $J_{7,6}$ 6.0 Hz, $J_{7,8}$15.2 Hz, H-7), 7.5–7.7 (3H, m, H-3, H-10, H-14), 0.26 (1H, dd, $J_{8,7}$15.2 Hz, $J_{8,9}$ 13.2 Hz, H-8), –0.93 (1H, dd, $J_{12,13}$12.0 Hz, $J_{12,11}$15.6 Hz, H-12), –0.96 (1H, dd, $J_{5,4}$12.4 Hz, $J_{5,6}$15.2 Hz, H-5). The "stable" isomer has structure 4 and at low temperature exists in the conformation shown. At higher temperatures there is rotation about the 7–8 *trans* bond (coalescence temperature *ca.* 40°). The spectrum at 70° clearly shows that 4 has undergone a fundamental (but reversible [6]) change. The signals due to the protons on the 7,8-*trans* double bond and the 9,10-*cis* double bond are broad. The remaining signals are sharp and their multiplicity indicates that at higher temperatures 4 exists in a more symmetrical conformation. ^{1}H nmr (δ, CD_2Cl_2, 70°, *inter alia*) 8.41 (2H, dd, $J_{4,3} = J_{13,14}$8.8 Hz, $J_{4,5} = J_{13,12}$12.0 Hz, H-4, H-13), 8.15 (2H, dd, $J_{6,5} = J_{11,12}$15.2 Hz, $J_{6,7} = J_{11,10}$6.4 Hz, H-6, H-11), 7.42 (2H, d, $J_{3,4} \doteq J_{14,13}$8.8 Hz, H-3, H-14), - 0.45 (2H, dd, $J_{5,6} = J_{12,11}$



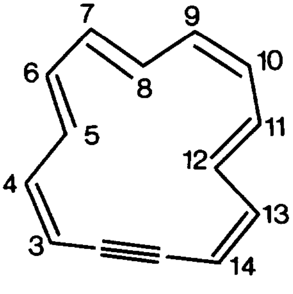


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Figure 2. ^{1}H nmr spectra of "stable" isomer 4 (200 MHz, CD_2Cl_2, temperatures as indicated).

15.2 Hz, $J_{5,4}$ = $J_{12,13}$12.0 Hz, H-5, H-12). In the previously reported[3,5] spectrum of 4 at 27° the broad band at *ca.* δ 0.5 had been neglected. This led to an incorrect assignment for the structure of 4.[7]

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References and Notes

1. Deceased 11 February 1981.
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3. F. Sondheimer, *Proc. Roy. Soc. A*, 1967, 297, 173.
4. The two isomers were most conveniently separated by centrifugally accelerated radial chromatography on a Chromatotron (Harrison Research instrument, model 7924) with a 1mm plate of $AgNO_3$ impregnated silica gel.
5. F. Sondheimer, I.C. Calder, J.A. Elix, Y. Gaoni, P.J. Garratt, K. Grohmann, G. di Maio, J. Meyer, M.V. Sargent, R. Wolovsky, *Chem. Soc. Spec. Publ.*, 1967, No. 21, 75.
6. The nmr spectra recorded after recooling the sample were identical to those recorded at low temperatures before the sample was heated.
7. The calculated ratio of the nine outer protons at low field to the two "remaining" inner protons at *ca.* δ -1.3 is 4.5:1 in reasonable agreement with the observed integration of 4.8:1.

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