The Conformational Inversion of 2,3:6,7-Dibenzo-derivatives of Cycloheptatriene, Tropone, Heptafulvene, Oxepin, Thiepin, and Azepin

By M. Nógrádi, W. D. Ollis,* and I. O. Sutherland
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary Comparison of the energy barriers to conformational inversion of the seven-membered rings in compounds of the types (I) and (II) shows that the change in delocalisation energy associated with the planar seven-membered rings is apparently due to increased Ar–C=C–Ar and Ar–X–Ar conjugation, and is not a special property of the cyclic conjugated system.

ALTHOUGH the 2,3:6,7-dibenzo-derivatives (I) and tribenzo-derivatives (II) of many seven-membered cyclic conjugated systems have been examined by both physical and chemical methods,[1] the established[1,2] non-planarity of many of these compounds makes the results obtained of limited relevance in a discussion of the assumed planar systems for which various types of π-electron calculations have been made.[3] The possibility of detecting increased π-electron delocalisation associated with planar seven-membered rings has now been investigated by the examination of the temperature-dependence of the n.m.r. spectra of suitable derivatives of types (I) and (II) containing prochiral[4] groupings.

The compounds (Ia—Ig) were synthesised using methods based upon reaction of the appropriate 10-lithio-derivatives with acetone, and the compounds (Ij, IIb, and IIc) were prepared by analogous methods to those already reported.[5] The results provided by the temperature-dependent n.m.r.

TABLE 1

N.m.r. spectral parameters (60 *and* 100 *MHz*) *and free energies of activation for conformational inversion*

Compound	Solvent[a]	Prochiral group	$\nu_A - \nu_B$ (Hz)	J_{AB} (Hz)	T_c (°K)	$\Delta G^\ddagger$ at T_c[b] (kcal. mole^{-1})
(Ia)	$CDCl_3$	CMe_2	2·6		317	17·5
(Ia)	$CDCl_3$	CH_2	11·1	12·2	340	17·1
(Ib)	$PhNO_2$	CMe_2	2·7		382	21·2
(Ic)	CS_2	CMe_2			<183	<9
(Id)	CS_2	CMe_2			<163	<9
(Ie)	C_6F_6	CMe_2	3·5		324	17·7
(If)	$CDCl_3:CS_2$ (1 : 2)	CMe_2	16		204	10·3
(Ig)	C_2HCl_5	CMe_2	2·4		389	21·7
(Ih)	CS_2	CH_2	*ca.* 11	12·5[d]	183	9·0
(Ih)[c]	CS_2	CH_2	15	12·5[d]	188	9·2
(Ij)	$CDCl_3:CS_2$ (1 : 3)	CH_2	14·3	12·5	222	11·0
(IIa)	Ph.Ph	CH_2	13·1	12·5	469	23·8
(IIa)[c]	Ph.Ph	CH_2	21·8	12·5	475	24·0
(IIb)[c]	Ph.Ph	CH_2	25·1	12·5	>473	>27·7
(IIb)[c]	Ph.Ph	CH_2 of Et	21·6	14·5	>473	>27·7
(IIc)[c]	Ph.Ph	CH_2 of Et	13·3	14·0	398	20·0

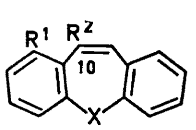
[a] The wide range of solvents used was necessary to give mobile solutions of sufficient concentration at the appropriate temperatures. The selection of solvents was also determined by the need to produce observable chemical shift nonequivalence between diastereotopic protons and methyl groups.

[b] Errors in $\Delta G^\ddagger$ are difficult to estimate, but should not exceed $\pm 0·5$ kcal.mole^{-1}.

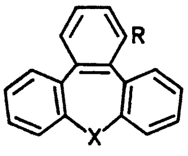
[c] Data from 100 MHz spectra; other spectra determined at 60 MHz.

[d] J_{AB} estimated by analogy with the compounds (Ij), (IIa), and (IIb) because the spectrum was not fully resolved at the lowest attainable temperature.

spectra of the compounds (Ia—Ij) and (IIa—IIc) are summarised in Table 1. These results refer to the coalescence temperatures, T_C,[6] associated with the signals of the diastereotopic methylene hydrogen atoms where X = CH_2 and N-CH_2Me, R¹ = CH_2Ph, and R = CH_2Me, and with the diastereotopic methyl groups where R² = CMe_2OH and CMe_2OMe.



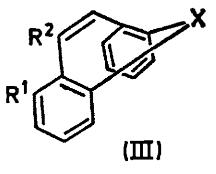
(I)



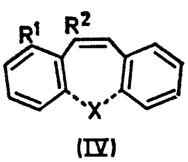
(II)

	R¹	R²	X
(a)	H	CMe_2OH	CH_2
(b)	H	CMe_2OH	$C{=}CH_2$
(c)	H	CMe_2OH	$C{=}O$
(d)	H	CMe_2OMe	$C{=}O$
(e)	H	CMe_2OH	S
(f)	H	CMe_2OH	O
(g)	H	CMe_2OH	NEt
(h)	H	H	CH_2
(j)	$PhCH_2$	H	CH_2

	R	X
(a)	H	CH_2
(b)	Et	CH_2
(c)	Et	CO



(III)



(IV)

The conformation (III) is chiral and its inversion is presumed to involve a planar achiral transition state in which three possible sources of π-electron delocalisation could operate more efficiently than in the non-planar ground state; these are (a) stilbenoid conjugation, (b) π–p or π–π aryl–X–aryl conjugation, and (c) conjugation associated with aromatic or anti-aromatic character in the seven-membered ring. The comparison of free energies of activation (see Table 1) leading to an estimation of the additional conjugation energies associated with (a), (b), and (c) required (i) the selection of a reference compound, (ii) the assessment of additional nonbonded interactions, and (iii) the estimation of the angle-strain energies, E_θ (rel.), resulting from the development of a planar transition state. 2,3 : 6,7-Dibenzocycloheptatriene (Ih, $\Delta G^\ddagger$ = 9·1 kcal. mole^{-1}) was chosen as the reference compound and the types of nonbonded interactions encountered in transition states for inversion are indicated in the Figure.

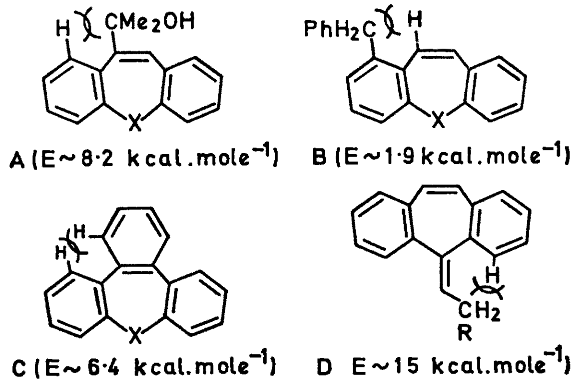


FIGURE. *Nonbonded interaction energies for situations of types A, B, C, and D.*

The indicated nonbonded interaction energies were assessed from the free energies of activation for conformational inversion of various pairs of derivatives: A (Ia and Ih); B (Ij and Ih); C (IIa and Ih); and D [(Vb and Va) and (Va and Ib); average value, *E ca.* 15 kcal.mole^{-1}]. The values for E_θ (rel.) given for each compound refer to the angle strains[7] in their planar transition states relative to the planar transition state for the reference compound (Ih).

TABLE 2

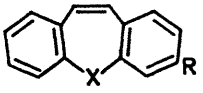
Comparison of the calculated inversion barrier [E_{inv} (calc.)] *and the observed inversion barriers* ($\Delta G^{\ddagger}$)

Compound	E_{θ} (rel.) (kcal.mole^{-1})	Additional nonbonded interaction in planar transition states (kcal.mole^{-1})	$E_{inv.}$ (calc.) (kcal.mole^{-1})	$\Delta G^{\ddagger}$ (kcal.mole^{-1})	$E_{inv.}$ (calc.) $-$ $\Delta G^{\ddagger}$ (kcal.mole^{-1})
(Ia)	0	A (8·2)	—	17·3	—
(Ib)	-2	A (8·2) + 2C (12·8)	28·1	21·2	7
(Ic)	-2	A (8·2)	15·3	<9	>6
(Ie)	$+4$	A (8·2)	21·3	17·7	4
(If)	$+1$	A (8·2)	18·3	10·3	8
(Ig)	$+1$	A (8·2) + 2B (3·8)	22·1	21·7	0
(Ih)	0	—	—	9·1	—
(Ij)	0	B (1·9)	—	11·0	—
(IIa)	$+2$	2C (12·8)	—	23·9	—
(IIb)	$+2$	C (6·4) + D (15)	32·5	$<27·7$	<5
(IIc)	0	C (6·4) + D (15)	30·5	20·0	11
(Va)	-2	C (6·4) + D (15)	28·4	22·6	6
(Vb)	-2	2D (30)	37·1	30·1	7

It has been assumed that there is the same change in the stilbenoid conjugation [see full lines in (IV)] in all cases.

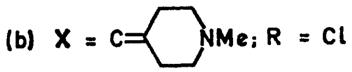
The compounds (Va) and (Vb) have been resolved[8] and their free energies of activation for conformational inversion determined[8] from their rates of racemisation. These results, which are included in Table 2, provide a comparison of $\Delta G^{\ddagger}$ values determined by the polarimetric and temperature-dependent n.m.r. methods.

Table 2 lists the calculated inversion barriers, $E_{inv.}$ (calc.), for compounds of the types (I), (II), and (V). The values of $E_{inv.}$ (calc.) for each compound were determined by summation of $\Delta G^{\ddagger}$ for the reference compound (Ih; $\Delta G^{\ddagger}$ = 9·1 kcal.mole^{-1}), the estimated change in angle strain energy, E_{θ} (rel.), and the relevant nonbonded interaction energies deduced for the situations A, B, C, and D (see Figure) or their equivalent. The difference between $E_{inv.}$ (calc.) and $\Delta G^{\ddagger}$ (see Table 2, last column) for each compound provides a measure of the stabilisation of the planar transition state associated with increased π–p or π–π aryl–X–aryl conjugation (b) and "aromatic" or "anti-aromatic" type conjugation (c) associated with a planar seven-membered ring. Table 2 shows that $E_{inv.}$(calc.) $-$ $\Delta G^{\ddagger}$ values usually fall within the range 4—8 kcal.mole^{-1}. This range is compatible with the increase in conjugation energy to be expected for π–p and π–π aryl–X–aryl conjugation and the compounds examined (excluding Ig and IIc) do not show a significant increase, or decrease, in delocalisation energy which could be a consequence of cyclic conjugation in the planar seven-membered ring.



(V)

(a) X = $C{=}CH{-}CH_2{-}CH_2{-}NMe_2$; R = H


(b) X = $C{=}C_5H_8NMe$; R = Cl

The result, $E_{inv.}$ (calc.) $-$ $\Delta G^{\ddagger}$ *ca.* 0 kcal.mole^{-1}, for the compound (Ig) is surprising in view of the p–π conjugation energy of 14·9 kcal.mole^{-1} estimated[9] for *N*-methyldiphenylamine. This difference may possibly be associated either with some anti-aromatic character in the planar azepin ring or it could involve the imposition of a geometry unfavourable for p-π conjugation in the transition state associated with the conformational inversion for the compound (Ig). The non-planar ground state conformation of the tribenztropone (IIc) is clearly required by the n.m.r. results (Table 1), but the value of $E_{inv.}$ (calc.) $-$ $\Delta G^{\ddagger}$ *ca.* 10 kcal. mole^{-1} does not indicate that its seven-membered tropone ring exhibits pronounced aromatic character in the planar transition state. This result coincides with the opinion recently expressed[10] that the stabilisation energy of tropone indicates that this system does not have significant aromatic character.

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[1] R. F. H. Manske and A. E. Ledingham, *J. Amer. Chem. Soc.*, 1950, **72**, 4797; E. D. Bergmann, D. Ginsburg, Y. Hirshberg, M. Mayot, A. Pullmann, and B. Pullman, *Bull. Soc. chim. France*, 1951, 697; F. A. L. Anet and P. M. G. Bavin, *Canad. J. Chem.*, 1956, **34**, 991; 1957, **35**, 1084; R. Huisgen, E. Laschtuvka, and F. Bayerlein, *Chem. Ber.*, 1960, **93**, 392; E. D. Bergmann and M. Rabinowitz, *J. Org. Chem.*, 1960, **25**, 827, 828; M. Rabinowitz, I. Agranat, and E. D. Bergmann, *Tetrahedron*, 1966, **22**, 225; E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 41.

[2] W. Tochtermann, C. Franke, and D. Schäfer, *Chem. Ber.*, 1968, **101**, 3122; W. Tochtermann, H. Küppers, and C. Franke, *ibid.*, p. 3808; H. Shimanouchi, T. Hata, and Y. Sasada, *Tetrahedron Letters*, 1968, 3573.

[3] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1961; N. C. Baird, *Canad. J. Chem.*, 1969, **47**, 3535.

[4] K. R. Hanson, *J. Amer. Chem. Soc.*, 1966, **88**, 2731.

[5] A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.*, 1951, **73**, 1673; W. Tochtermann, K. Oppenländer, and U. Walter, *Chem. Ber.*, 1964, **97**, 1329; G. J. B. Corts and W. T. Nauta, *Rec. Trav. chim.*, 1966, **85**, 389; V. Seidlova and M. Protiva, *Coll. Czech. Chem. Comm.*, 1967, **32**, 2826; W. Treibs and H.-J. Klinkhammer, *Chem. Ber.*, 1951, **84**, 171.

[6] G. Binsch, *Topics Stereochem.*, 1968, **3**, 97.

[7] F. H. Westheimer in "Steric Effects in Organic Chemistry," ed. M. S. Newman, Wiley, New York, 1956, p. 523; E. L. Eliel, M. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, 1965, p. 433.

[8] A. Ebnöther, E. Jucker, and A. Stoll, *Helv. Chim. Acta*, 1965, **48**, 1237.

[9] I. P. Romm, E. N. Guryanova, and K. A. Kocheshkov, *Tetrahedron*, 1969, **25**, 2455.

[10] D. J. Bertelli and T. G. Andrews, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 5280, 5286.