Conformation of Triphenyl-*s*-Triazine

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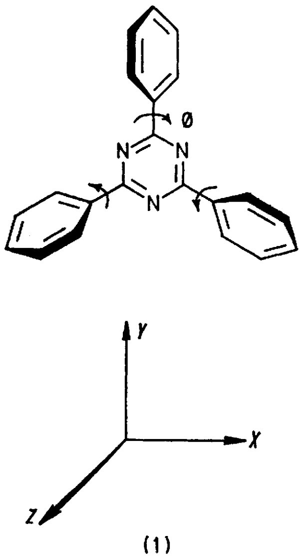
The infinite dilution molar Kerr constant of triphenyl-*s*-triazine as a solute in dioxan at 298 K is analysed to provide evidence concerning the molecular conformation. Structures having equivalent rotations of the phenyl groups about the inter-ring bonds are considered and its is found that the dihedral angle, ϕ, lies within the range $0 \leqslant \phi \leqslant 27°$. The conformational preferences of triphenyl-*s*-triazine and 1,3,5-triphenylbenzene are compared.

A COMPARISON of the conformations of the structurally analogous molecules 1,3,5-triphenylbenzene and triphenyl-*s*-triazine (1) would be expected to reflect the important differences between the benzene and *s*-triazine ring systems.[1] Although the conformational preference of 1,3,5-triphenylbenzene in various physical states has been established,[2-4] only the solid-state structure[5] of triphenyl-*s*-triazine is known with certainty. We here report and analyse the infinite dilution molar Kerr constant of triphenyl-*s*-triazine as a solute in dioxan at 298 K. The results complement previous i.r.[6,7] and n.m.r.[8] spectral studies of this molecule.



(1)

EXPERIMENTAL

Materials.—Triphenyl-*s*-triazine was recrystallized from toluene to yield needles, m.p. 229—230 °C. Analytical reagent grade dioxan was purified by passage through a

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[1] A. Albert, 'Heterocyclic Chemistry,' Athlone Press, London, 1968.

[2] M. S. Farag, *Acta Cryst.*, 1954, **7**, 117.

[3] O. Bastiansen, *Acta Chem. Scand.*, 1952, **6**, 205.

[4] C. L. Cheng, D. S. N. Murthy, and G. L. D. Ritchie, *J.C.S. Faraday II*, 1972, 1679.

[5] A. Damiani, E. Giglio, and A. Ripamonti, *Acta Cryst.*, 1965, **19**, 161.

[6] R. D. Spencer, *Spectrochim. Acta*, 1965, **21**, 1543.

[7] H. F. Shurvell, *J. chim. Phys.*, 1965, **62**, 1027.

[8] V. M. S. Gil and A. M. P. Pereira, *Tetrahedron*, 1971, **27**, 5619.

neutral alumina column and stored over molecular sieves (0.4 nm; 30 g for 2 l).

Apparatus, Procedures, and Results.—Procedures for obtaining infinite dilution molar refractions and Kerr constants from observations of incremental relative permittivities, densities, refractive indices, and electric birefringences of dilute solutions in non-dipolar solvents are described elsewhere;[9] details of symbols, solvent constants, conversion factors for units, *etc.* are also on record.[9,10] Because of the low solubility of triphenyl-*s*-triazine in dioxan the ten solutions examined had weight fraction concentrations of $<0.5\%$ w/w (*i.e.*, $10^2 w_2 < 0.5$). The results are summarized in Table 1.

TABLE 1

Molar refraction and molar Kerr constant of triphenyl-*s*-triazine at 298 K and 632.8 nm from observations on dilute solutions in dioxan [a]

$\alpha\varepsilon_1$	0.15 ± 0.23
β	0.132 ± 0.001
γ	0.172 ± 0.005
δ	53.5 ± 2.7
R_D/cm^3	104.9 ± 1.2
$10^{27}\infty/(_mK_2)$/m^5 V^{-2} mol^{-1}	229 ± 11

[a] See refs. 9 and 10 for explanation of symbols.

DISCUSSION

Analysis of Kerr Constant and Molecular Conformation.—Application of the Kerr effect [9] to conformational problems is based on the bond-additivity model for the molecular polarisability, and involves comparison of the observed Kerr constant with those predicted for possible stereostructures of the molecule. In the case of triphenyl-*s*-triazine (1) we considered the uniplanar (ϕ 0°) reference structure and conformations derivable from this by equivalent rotations of the phenyl groups about the inter-ring C–C bonds; all such 'propeller' structures therefore possess a C_3-rotation axis. It is easily shown that the molar Kerr constant of any such conformation, defined by the dihedral angle ϕ, is given by the general expression (1) in which $\Delta\alpha^{CC}$, $\Delta\alpha^{Tr}$, and $\Delta\alpha^{Ph}$ are the

$$_mK = (N_A/81\varepsilon_0)\{\gamma^k + (9/20\,kT)\,[\Delta\alpha^{CC} + (2/3)\Delta\alpha^{Tr} + \Delta\alpha^{Ph}(3\cos^2\phi - 1)]^2\} \quad (1)$$

polarisability anisotropies (*i.e.* $\alpha_L - \alpha_V$) for the C–C bond, the triazinetriyl (C_3N_3) group, and the phenyl group. The mean second molecular hyperpolarisability, γ^k, of triphenyl-*s*-triazine was roughly estimated as being four times the corresponding value for benzene;[11] the contribution (*ca.* 3×10^{-27} m^5 V^{-2} mol^{-1}) which γ^k makes to the Kerr constant of this molecule is therefore probably almost negligible. Recently reported [10,12] anisotropic polarisabilities for benzene and *s*-triazine at λ 632.8 nm were used, together with standard values for the C–C and C–H bonds (Table 2).

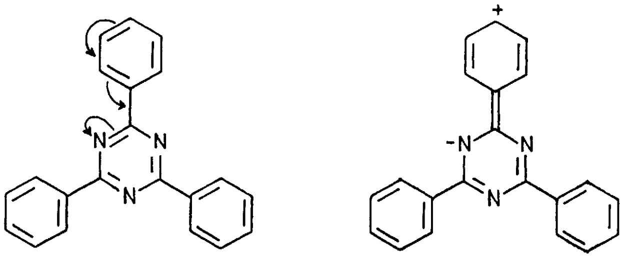
A serious difficulty in applying the bond additivity model to triphenyl-*s*-triazine arises from the fact that the observed molar refraction (104.9 cm^3) considerably exceeds the value (91.4 cm^3) calculated from known group refractions, a disparity indicative of enhanced electron delocalization. The corresponding polarisability exaltation, which must be included in the calculations, is even greater than the unusually large value found for 1,3,5-triphenylbenzene.[4] Conjugative interactions would be expected to be more pronounced in triphenyl-*s*-triazine than in 1,3,5-triphenylbenzene: the nitrogen atoms have the effect of localizing charge, leaving the carbon atoms electron deficient so that rearrangements as in (2) are facilitated. Reduced steric repulsion in triphenyl-*s*-triazine would also favour such structures.

TABLE 2

Polarisability components (expressed as $10^{40}\alpha$/C m^2 V^{-1}) for molecules and bonds

	α_L	α_T	α_V
Benzene [a,b]	13.0	13.0	8.8
s-Triazine [a,c]	9.8	9.8	5.0
C–H [d]	0.72	0.72	0.72
C–C [d]	1.08	0.29	0.29

[a] λ 632.8 nm. [b] Ref. 10. [c] Ref. 12. [d] Standard values from ref. 9 for λ 589 nm, assumed applicable at λ 632.8 nm.



(2)

The crystal structure [5] of triphenyl-*s*-triazine showed that in the solid state this molecule is not uniplanar; the three phenyl rings are rotated from the plane of the triazine ring through different angles and in opposite senses (±ϕ 7—11°). However i.r. spectra [6,7] of both solid and solution states were interpreted as providing unequivocal evidence for the uniplanar conformation. From a study [8] of the ^{1}H n.m.r. chemical shifts of triphenyl- and tri-(2-pyridyl)-*s*-triazine it was deduced that the latter molecule is more nearly uniplanar than the former, for which it was concluded only that $\phi < 45°$.

Because of the uncertainty associated with the directional apportionment of the large polarisability exaltation we attempted only to define extreme upper and lower limits for ϕ. Since the exaltation is primarily an indication of extended π-electron delocalization, it would be expected predominantly to augment the molecular polarisability in the XY-plane, shown in (1). Calculations established that if the exaltation were distributed

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[9] C. G. Le Fèvre and R. J. W. Le Fèvre, in 'Techniques of Chemistry,' ed. A. Weissberger, Wiley–Interscience, New York, 1972, vol. 1, part IIIC, ch. 6, p. 399.

[10] M. R. Battaglia and G. L. D. Ritchie, *J.C.S. Faraday II*, 1977, 209.

[11] M. P. Bogaard, A. D. Buckingham, and G. L. D. Ritchie, *Mol. Phys.*, 1970, **18**, 575.

[12] M. R. Battaglia and G. L. D. Ritchie, *Mol. Phys.*, 1976, **32**, 1481; *J.C.S. Perkin II*, 1977, 897.

in the ratio $\Delta\alpha_{XX} : \Delta\alpha_{YY} : \Delta\alpha_{ZZ} = 0.43 : 0.43 : 0.14$ (which is reasonable), the predicted Kerr constant for ϕ 0° is equal to the observed value. Therefore, on the present evidence, the uniplanar conformation cannot be excluded, and ϕ 0° is the *minimum* permissible dihedral angle. The *maximum* value of ϕ is obtained, as can be seen from equation (1), when the exaltation is assigned completely to the XY-plane ($\Delta\alpha_{XX} : \Delta\alpha_{YY} : \Delta\alpha_{ZZ} = 0.50 : 0.50 : 0$); this has the effect of substantially increasing $\Delta\alpha^{Tr}$ and $\Delta\alpha^{CC}$ so that a much larger dihedral angle (ϕ 27°) is required for agreement between observed and calculated Kerr constants. We therefore conclude that $0 \leqslant \phi \leqslant 27°$, the rather wide range of possible values arising from the very large polarisability exaltation exhibited by this molecule.

Conclusions.—The result for triphenyl-*s*-triazine ($0° \leqslant \phi \leqslant 27°$) may be compared with conformational evidence concerning 1,3,5-triphenylbenzene. In the solid state [2] the latter molecule is non-uniplanar with $\pm\phi$ 24—34°; for the vapour, electron diffraction [3] indicated equivalent rotations of ϕ 46° for each phenyl group; and for the solution state Kerr and Cotton–Mouton effect measurements [4] yielded ϕ 35 ± 5°. The evidence suggests, therefore, that the dihedral angle in triphenyl-*s*-triazine is significantly smaller than that in 1,3,5-triphenylbenzene. Two main factors would appear to co-operate in producing this result: first a *steric effect*, arising from the probability that the *ortho-ortho* HC · · · N interaction is less repulsive than the corresponding HC · · · CH interaction, as shown by Murrell *et al.*[13] from ^{1}H n.m.r. spectra of azabiphenyls; and also enhanced *conjugative interactions* between the *s*-triazine and phenyl rings.

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[13] J. N. Murrell, V. M. S. Gil, and F. B. Van Duijneveldt, *Rec. Trav. chim.*, 1965, **84**, 1399.