810. *Molecular Polarisability: The Dipole Moment, Molar Kerr Constant, and Space Formula of Tröger's Base as a Solute in Benzene.*

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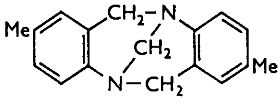
In benzene as solvent, Tröger's base has a dipole moment of $1{\cdot}0_1$ D, and a molar Kerr constant of -17×10^{-12}. Scale models (Barton type) suggest three possible conformations for which the calculated molar Kerr constants are -46, -14, and -52×10^{-12}, respectively. It is concluded that as a solute Tröger's base exists largely in the second conformation in which the Ar-rings are nearly perpendicular to one another and the $CH_2{\cdot}N{\cdot}CH_2{\cdot}N$ units are non-planar in a way resembling the $-[CH_2]_4-$ unit in *trans*-tetralin.

The base $C_{17}H_{18}N_2$, isolated in 1887 by Tröger[1] from *p*-toluidine and formaldehyde, was shown by Spielman[2] in 1935 to have structure (I) in preference to others which had been previously suggested.[1,3] Prelog and Wieland[4] noted that the model of (I) was dissymmetric and effected the first optical resolution by chromatographic adsorption. More recently Wepster[5] has considered its spatial formulation in connection with spectral studies of mesomerism among aromatic amines; he observes that with usual interatomic distances and intervalency angles two almost strain-free constructions are possible: configurations T and C. In T the Ar-rings are nearly perpendicular to each other; this is the "*trans*"-form, depicted in Fig. 1 where the Ar-rings are represented as hexagons, the two nitrogen atoms are labelled N_3, N_4, and the two methyl groups attached to the Ar-rings *para* to the nitrogen atoms are not shown. The nitrogen atoms and some of the carbon atoms are labelled to relate to Figs. 3 and 4. In configuration C the Ar-rings are in an "extended" disposition (Fig. 2 illustrates this model). If, in $C_6H_5{\cdot}NX_2$, the X–X line makes an angle ϕ with the C_6H_5 plane, then, for Tröger's base as configuration T, ϕ is *ca.* 45°, while as configuration C, it is *ca.* 80°; further, the heterocyclic rings are not flat in either arrangement, but in relation to the annellated C_6 rings have conformations in forms T and C



(I)

Fig. 1.

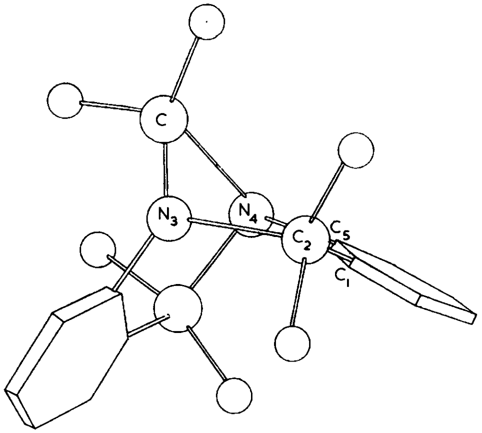
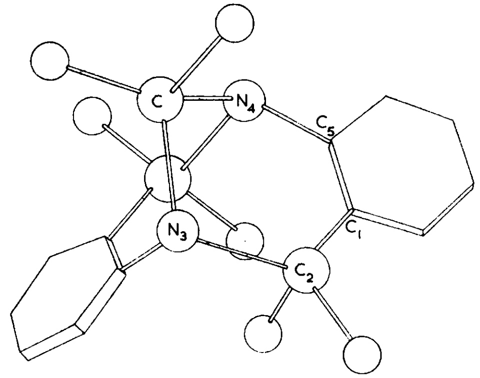


Fig. 2.



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[1] Tröger, *J. prakt. Chem.*, 1887, **36**, 227.
[2] Spielman, *J. Amer. Chem. Soc.*, 1935, **57**, 583.
[3] Eisner and Wagner, *J. Amer. Chem. Soc.*, 1934, **56**, 1938.
[4] Prelog and Wieland, *Helv. Chim. Acta*, 1944, **27**, 1127.
[5] Wepster, *Rec. Trav. chim.*, 1953, **72**, 661.

resembling those[6] of the $-[CH_2]_4-$ portions of *trans*- and *cis*-tetralin respectively. Wepster[5] notes that the models show Tröger's base to be " definitely not absolutely rigid " and that " configurations T and C can be converted into each other fairly easily," although some angle-strain has to be overcome during the process; he concludes " there can be no doubt that T is several kilocalories more stable than C."

Whether Tröger's base as a solute is a single form or a mixture seemed at the outset to be a question probably answerable by considerations of molecular polarisability.

Experimental.—Tröger's base was prepared from hydrochloric acid saturated with hydrogen chloride (70 c.c.), 40% aqueous formaldehyde (70 c.c.), and *p*-toluidine (20 g.) in ethanol (200 c.c.), essentially by Goecke's method.[7] Yields were low and variable (cf. Wagner's comments on the reactions involved [8]); after many recrystallisations from aqueous alcohol (charcoal) about 4 g. of white needles, m. p. 135—136°, were obtained.

Infrared spectra were taken of mulls in Nujol and hexachlorobutadiene; absorptions (cm.$^{-1}$) due to Tröger's base were:

1495—1497s
1440w
1412w
1328m
1225w
1210m
1195w/m
1163w
1142w/m
1112m
1097m
1065m
1040vw
963m/s
956sh
942sh
898m
873w
865w
830s
747w
740w
713w
689w

Apart from absorptions characteristic of C–H links (2960—2910, and 2855 cm.$^{-1}$), the substance was transparent over the region associated with N–H groups, a fact which formally invalidates the structure proposed by Eisner and Wagner; [3] likewise the absence of absorption between 1600 and 1700 cm.$^{-1}$, where C=N should [9] reveal itself, is against Tröger's original formula, $(Me{\cdot}C_6H_4{\cdot}N{=}CH)_2CH_2$.

Measurements of the dipole moment, molecular refraction, and molar Kerr constant of Tröger's base in benzene, obtained by methods described in refs. 10—12, are summarised under the usual headings in Table 1. The various constants required for benzene at 25° are:

$\varepsilon_1 = 2{\cdot}2725$
$d_1 = 0{\cdot}87378$
$B_1 = 0{\cdot}410 \times 10^{-7}$
$(n_D)_1 = 1{\cdot}4973$
$p_1 = 0{\cdot}34086$
$C = 0{\cdot}18809$
$H = 2{\cdot}114$
$J = 0{\cdot}4681$
${}_sK_1 = 7{\cdot}56 \times 10^{-14}$

Definitions of symbols used, and details of the calculations involved, are given in ref. 11, pp. 280—283, and ref. 12, pp. 2486—2490.

TABLE 1. *Incremental dielectric constants, densities, refractive indexes, and electric birefringences for solutions containing weight fractions w_2 of Tröger's base in benzene at 25°.*

10^5w_2	906	2689	3122	3357	3937	4367	4584
$10^4\Delta\varepsilon$	66	205	255	262	323	358	391
$10^5\Delta d$	163	547	620	721	843	901	934
$10^4\Delta n$	6	25	29	36	39	44	48
10^5w_2	709	1157	1692	1943	3039	3825	*
$10^4\Delta\varepsilon$	57	79	129	165	237	321	
$10^5\Delta d$	147	228	355	414	637	715	
10^5w_2	3357	4551	4584	4941	5397		
$-10^{11}\Delta B$	180	221	237	250	272		

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}806_2$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}204_5$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}076_6$; $\Sigma\Delta B/\Sigma w_2 = -0{\cdot}508_1$; and $\Sigma(n_{12}^2 - n_1^2)/\Sigma w_2 = 0{\cdot}296_7$.

* Determinations made by Mr. D. D. Brown, on another preparation, during 1949.

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[6] de Jong, quoted in ref. 5 from Thesis, Amsterdam, 1951.

[7] Goecke, *Z. Elektrochem.*, 1903, **9**, 473.

[8] Wagner, *J. Org. Chem.*, 1954, **19**, 1862.

[9] Fabian and Legrand, *Bull. Soc. chim. France*, 1956, 1461.

[10] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. II.

[11] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

[12] Le Fèvre and Le Fèvre, Chap. 36 in " Physical Methods of Organic Chemistry," Interscience Publ., Inc., New York, 3rd edn., 1960.

In the equations: ${}_{\infty}P_2 = M_2[p_1(1 - \beta) + C\alpha\varepsilon_1]$ and ${}_{\infty}({}_{\mathrm{m}}K_2) = M_2[{}_{\mathrm{s}}K_1(1 - \beta + \gamma + \delta - H\gamma - J\alpha\varepsilon_1)]$ we have, from the tabulated data, $\alpha\varepsilon_1 = 0{\cdot}806_2$, $\beta = 0{\cdot}234_0$, $\gamma = 0{\cdot}051_2$, $\delta = -1{\cdot}23_9$, so that ${}_{\infty}P_2 = 103{\cdot}3$ c.c. and ${}_{\infty}({}_{\mathrm{m}}K_2) = -17{\cdot}2 \times 10^{-12}$, $R_2 = 78{\cdot}4$ c.c. and $\mu = 1{\cdot}01$ D (if the distortion polarisation is $1{\cdot}05R_{\mathrm{D}}$).

Discussion.—As a preliminary we have examined Barton-type models of the base (I), using inter-centre distances:[13] C–C, 1·54 Å, C_{Ar}–C_{Ar}, 1·39 Å, and C–N, 1·47 Å. A third conformation, in which all the carbon atoms to the right of the N···N line lie in one plane and all those to the left in another, is thus revealed as not excessively strained (although this conformation is not illustrated, Fig. 3 serves to explain further its characteristics). This conformation we term form P (= planar). Our procedure has been to calculate the principal polarisabilities b_1, b_2, and b_3 expected for the three conformations, thence to compute the corresponding molar Kerr constants, and finally to compare the ${}_{\mathrm{m}}K$'s so produced with that determined by experiment.

FIG. 3.

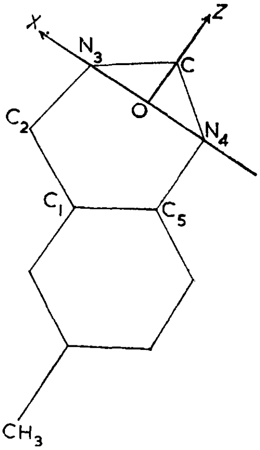
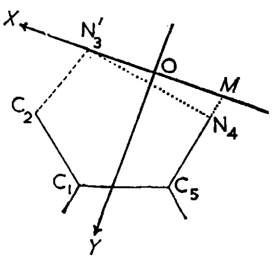


FIG. 4.



Anisotropic bond and group polarisabilities required were:[11,12,14]

	C–H	C–C	C–N	C_6H_3
$10^{23}b_L$	0·064	0·099	0·057	0·928
$10^{23}b_T$	0·064	0·027	0·069	0·928
$10^{23}b_V$	0·064	0·027	0·069	0·544

The various inter-bond angles also needed were obtained where possible by calculation, and otherwise by direct measurement of the models.

Fig. 3 shows part of structure P. The plane N_3CN_4 is assumed to be at 120° to each of the planes containing all the carbon and nitrogen atoms of the molecule, other than the carbon of the apical methylene group. With the angles $C_1C_2N_3$, $C_5C_1C_2$, and $N_4C_5C_1$ at 109° 28′, 120°, and 120°, respectively, that for N_3CN_4 becomes 101° 3′ and the centre–centre distance from N_3 to N_4 is 2·27 Å. (Such an N–C–N angle is smaller than normal,[13] cf. 108° ± 4° in NMe_3, but not impossible, cf. 99° in nickel phthalocyanine[13] or 95° in potassium benzylpenicillin[13]). Arbitrary axes OX, OY, and OZ (O being midway between N_3 and N_4) are imposed on the structure, with OX along N_4ON_3, OZ along OC, and OY, perpendicular to OX and OZ; b_{XX}, b_{XY}, b_{XZ}, b_{YX}, b_{YY}, etc., are then evaluated, and b_1 b_2, and b_3 obtained, together with the nine direction cosines locating them in the OX, OY, OZ framework, by the method outlined in ref. 12, p. 2486.

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[13] Sutton, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* No. 11, 1958.

[14] Aroney and Le Fèvre, *J.*, 1958, 3002.

Results emerge as follows:

	Direction cosines with			
	OX	OY	OZ	
$10^{23}b_1 = 3{\cdot}25_8$	$+0{\cdot}9624$	$-0{\cdot}2715$	0	$\mu_1 = \mu_2 = 0, \mu_3 = 1{\cdot}01$ D, and $_{\mathrm{m}}K$ calc. = -46×10^{-12}
$10^{23}b_2 = 3{\cdot}03_5$	$+0{\cdot}2715$	$+0{\cdot}9624$	0	
$10^{23}b_3 = 2{\cdot}59_3$	0	0	$+1$	

Fig. 4 shows part of structure T, which differs from P in that, while atoms C_2 and N_4 remain in-plane with the Ar-ring, N_3 is out-of-plane and situated below this plane (if the apical carbon is regarded as above it). Measurement of the model gives 15° as the angle which the bond C_2N_3 makes with its projection C_2N_3' on to the plane $C_2C_1C_5N_4$. Since the two Ar-ring-planes appear to be at 90° to one another, the line of intersection of these planes defines the OX direction (Fig. 4). The mid-point O of MN_3' is the origin of our arbitrary axes so that OY is in the plane of one Ar-ring and OZ in that of the other. Calculation as before gives:

	Direction cosines with			
	OX	OY	OZ	
$10^{23}b_1 = 3{\cdot}21_7$	$+0{\cdot}9938$	$-0{\cdot}0789$	$-0{\cdot}0789$	$\mu_1 = \mu_2 = 0, \mu_3 = 1{\cdot}01$ D, and $_{\mathrm{m}}K$ calc. = -14×10^{-12}
$10^{23}b_2 = 2{\cdot}82_8$	$+0{\cdot}1116$	$+0{\cdot}7027$	$+0{\cdot}7027$	
$10^{23}b_3 = 2{\cdot}84_0$	0	$-0{\cdot}7071$	$+0{\cdot}7071$	

In structure C the Ar-rings are " extended " more than in T, and their planes intersect at about 45°; atom N_3 is out-of-plane with its *p*-tolyl nucleus and on the same side as is the apical carbon. The line C_2N_4 is chosen as the OX axis, with OY in the plane of the nearer Ar-ring, and OZ mutually perpendicular to OX and OY. The angles between these axes and the various bonds in the molecule are measured by hand (experience of repeated assembly, dismantling, and reassembly of Barton models shows that these can be thus estimated within 1°). For conformation C we find:

	Direction cosines with			
	OX	OY	OZ	
$10^{23}b_1 = 3{\cdot}05_8$	$+0{\cdot}8621$	$-0{\cdot}2655$	$+0{\cdot}4316$	$\mu_1 = 0{\cdot}100$ D, $\mu_2 = 0{\cdot}028$ D, $\mu_3 = 1{\cdot}00$ D, and $_{\mathrm{m}}K$ calc. $= -52 \times 10^{-12}$
$10^{23}b_2 = 3{\cdot}33_6$	$+0{\cdot}3223$	$+0{\cdot}9446$	$-0{\cdot}0626$	
$10^{23}b_3 = 2{\cdot}49_1$	$-0{\cdot}3910$	$+0{\cdot}1930$	$+0{\cdot}8999$	

Finally, as a check on our calculations above, we note that the sums $(b_1 + b_2 + b_3)$ for conformations P, T, or C are $8{\cdot}88_5 \times 10^{-23}$ c.c.; this corresponds to an electronic polarisation of 74·7 c.c. The observed R_{D} is 78·4 c.c. from which, if (as is often the case) $_{\mathrm{E}}P$ = *ca.* $0{\cdot}95R_{\mathrm{D}}$, $_{\mathrm{E}}P$ is 74·5 c.c.

Since the molar Kerr constants expected for the P, T, and C conformations are respectively -46, -14, and -52×10^{-12}, and the value found by experiment is -17×10^{-12} Tröger's base as a solute in benzene evidently exists largely as form T; on the data quoted a content of form T of 90% at least is indicated.

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