720. *Molecular Polarisability. Conformations of Certain Arylamines, -hydrazines, etc.*

By M. ARONEY and R. J. W. LE FÈVRE.

The molar Kerr constants, dipole moments, refractivities, etc., are reported for Ph·NH·NH$_2$, (Ph·NH)$_2$, *p*-NH$_2$·C$_6$H$_4$·NH$_2$, (*p*-NH$_2$·C$_6$H$_4$)$_2$, NHPh$_2$, NPh$_3$, CHPh$_3$, and cyclohexylamine. The apparent (or average) conformations indicated by these measurements for each species as a solute are discussed.

THIS paper is connected with four others[1] in which, *inter alia*, polarisability ellipsoids for the C–N and N–H bonds were specified and applied to a number of nitrogen-containing molecules. Hydrazine and the eight substances of Table 1 and 2 have now been examined by measurements of Kerr constants and dipole moments. Conclusions regarding their apparent conformations as solutes are given under " Discussion."

EXPERIMENTAL

Apparatus, Procedures, etc.—These have been as fully described before.[1-3] Symbols and methods of calculation used in this paper are defined and explained in refs. 2 and 3. Sodium-dried benzene or calcium chloride-dried carbon tetrachloride was the solvent employed. Solutes were redistilled or recrystallised, as appropriate, immediately before solutions were made up. Hydrazine, which presented difficulties, is dealt with separately below. Observations are listed in Table 1; when $w_2 = 0$ the following solvent properties apply: for benzene,

TABLE 1. *Kerr effects, polarisations, etc., for solutions in benzene or carbon tetrachloride at 25°.*

Phenylhydrazine in benzene.

10^5w_2 ...	841	1293	1882	2458	3507	4286	5149
$10^7\Delta B$ ...	0·010	0·014	0·022	0·032	0·042	0·054	0·067

whence $10^7\Delta B = 1{\cdot}15w_2 + 2{\cdot}49w_2^2$.

10^5w_2 ...	418	796	1103	1641	2349	2664	3905	3919
ε^{25}	2·2859	2·2983	2·3075	2·3243	2·3465	2·3559	2·3952	2·3958
d_4^{25}	0·8745	—	0·8757	0·8766	0·8779	0·8786	0·8807	0·8810
10^5w_2 ...	1725	2881	3325	5111				
Δn	0·0016	0·0027	0·0032	0·0048				

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}17$, $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}175$, $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}094$.

Hydrazobenzene in benzene.

10^5w_2 ...	1273	1509	1742	1941	2113	2459
$10^7\Delta B$ ...	−0·028	−0·033	−0·039	−0·042	−0·046	−0·054
Δn	—	—	0·0019	—	—	0·0029

whence $10^7\Delta B = -2{\cdot}22w_2 + 1{\cdot}16w_2^2$, $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}113$.

10^5w_2 ...	562	1273	1509	1940	2163	2614
ε^{25}	2·2845	2·2997	2·3047	2·3136	2·3188	2·3282
d_4^{25}	0·87493	0·87640	0·87691	0·87776	0·87829	0·87925

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}13$, $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}207$.

p-*Phenylenediamine in benzene.*

10^5w_2 ...	239	253	257	290	306	314	345
$10^7\Delta B$ ...	−0·008	—	−0·009	−0·010	−0·012	−0·012	−0·014
Δn	0·0003	0·0003	0·0003	—	—	—	—

whence $\Sigma\Delta B/\Sigma w_2 = -3{\cdot}67$, $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}121$.

10^5w_2 ...	228	239	253	257	306	345
ε^{25}	2·2794	2·2795	2·2798	2·2798	2·2817	2·2830
d_4^{25}	0·87427	0·87432	0·87436	0·87436	0·87444	0·87455

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}95$, $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}223$.

---

[1] Aroney and Le Fèvre, *J.*, 1956, 2775; *Proc. Chem. Soc.*, 1958, 82; *J.*, 1958, 3002; *J.*, 1960, 2161.
[2] Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577; *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[3] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. II.

TABLE 1. (*Continued.*)

Benzidine in benzene.

10^5w_2 ...	436	726	791	905	953	1028	1071	1098
$10^7\Delta B$ ...	−0·011	−0·017	—	−0·021	−0·022	−0·024	−0·024	−0·026
Δn	—	—	0·0014	—	—	0·0018	0·0019	0·0020

whence $\sum\Delta B/\sum w_2 = -2{\cdot}35$, $\sum\Delta n/\sum w_2 = 0{\cdot}178$.

10^5w_2 ...	700	763	791	820	980	1027	1097	1186
ε^{25}	2·2862	2·2880	2·2883	2·2891	2·2921	2·2935	2·2944	2·2979
d_4^{25}	0·87552	0·87564	0·87575	0·87580	0·87624	0·87631	0·87638	0·87658

whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}02$, $\sum\Delta d/\sum w_2 = 0{\cdot}245$.

Diphenylamine in benzene.

10^5w_2 ...	1440	1831	3376	4256	5703	6194
$10^7\Delta B$ ...	0·020	0·021	0·038	0·052	0·066	0·072

whence $10^7\Delta B = 1{\cdot}23_3w_2 - 1{\cdot}19w_2^2$.

10^5w_2 ...	1127	1835	3472	4591
Δn	0·0014	0·0024	0·0046	0·0060

whence $\sum\Delta n/\sum w_2 = 0{\cdot}131$.

10^5w_2 ...	633	1127	1519	1835	2171	3472	4591
ε^{25}	2·2794	2·2850	2·2895	2·2928	2·2968	2·3116	2·3255
d_4^{25}	0·87498	0·87586	0·87631	0·87730	0·87780	0·88033	—

whence $\sum\Delta\varepsilon/\sum w_2 = 1{\cdot}12$, $\sum\Delta d/\sum w_2 = 0{\cdot}183$.

Triphenylamine in benzene.

10^5w_2 ...	1440	3674	5279	5618	7918	11,023
$10^7\Delta B$ ...	0·010	0·022	0·034	0·036	0·051	0·076

whence $10^7\Delta B = 0{\cdot}584w_2 + 0{\cdot}930w_2^2$.

10^5w_2 ...	7643	8366
Δn_{D}	0·01015	0·01168
Δn_{G} ...	0·01238	0·01398

whence $\sum\Delta n_{\mathrm{D}}/\sum w_2 = 0{\cdot}164$.

10^5w_2 ...	774	1086	1236	1350	1838	2952
ε^{25}	2·2773	2·2791	2·2797	2·2811	2·2831	2·2908
d_4^{25}	0·87530	0·87593	0·87618	0·87635	0·87728	0·87949

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}609$, $\sum\Delta d/\sum w_2 = 0{\cdot}194$.

Triphenylmethane in carbon tetrachloride.

10^5w_2 ...	766	1679	1884	3560
$10^7\Delta B$ ...	0·002	0·004	0·005	0·009
Δn	0·0020	0·0042	0·0049	0·0089

whence $\sum\Delta B/\sum w_2 = 0{\cdot}255$, $\sum\Delta n/\sum w_2 = 0{\cdot}255$.

10^5w_2 ...	421	766	1679	1884	3560
ε^{25}	—	2·2328	2·2392	2·2419	2·2522
d_4^{25}	1·58156	1·57926	—	1·57167	1·55952

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}746$, $\sum\Delta d/\sum w_2 = -0{\cdot}696$.

Cyclohexylamine in benzene.

10^5w_2 ...	1344	2048	2879	3524	3993	4466	5878	6661
$10^7\Delta B$ ...	0·006	0·009	0·012	0·013	0·015	0·016	0·018	0·020
Δn	—	−0·0010	—	—	—	−0·0023	−0·0028	—
10^5w_2 ...	7376	11,972	15,920	19,174	26,422	28,693	33,819	
$10^7\Delta B$ ...	0·020	0·022	0·010	−0·005	−0·042	−0·051	−0·097	
Δn	−0·0036	−0·0056	—	—	−0·0123	—	—	

For concentrations up to $w_2 = 4466 \times 10^{-5}$ (inclusive)

$10^7\Delta B = 0{\cdot}500w_2 - 3{\cdot}24w_2^2$, $\sum\Delta n/\sum w_2 = -0{\cdot}049$.

10^5w_2 ...	2048	2879	4466	5878	7376	11,972	15,920
ε^{25}	2·3114	—	2·3543	2·3807	2·4085	2·4908	2·5676
d_4^{25}	0·87342	0·87325	0·87303	0·87274	0·87252	0·87174	0·87088

whence $\sum\Delta\varepsilon/\sum w_2 = 1{\cdot}86$, $\sum\Delta d/\sum w_2 = -0{\cdot}0175$.

$\varepsilon = 2{\cdot}2725$, $d = 0{\cdot}87378$, $n_D = 1{\cdot}4973$, $B = 0{\cdot}410 \times 10^{-7}$; for carbon tetrachloride, $\varepsilon = 2{\cdot}2270$, $d = 1{\cdot}5845$, $n_D = 1{\cdot}4575$, $B = 0{\cdot}070 \times 10^{-7}$. When Δ precedes a symbol, a difference between solution and solvent is implied, *e.g.*, $\Delta\varepsilon = \varepsilon_{12} - \varepsilon_1$. Table 2 contains the molar Kerr constants and total polarisations at infinite dilution, together with dipole moments, computed from the measurements recorded in Table 1.

Previous Determinations related to Table 2.—The following dipole moments (D) have been recorded (numerals in parentheses being references), for benzene solutions unless otherwise stated: Ph·NH·NH$_2$, 1·65—1·79 (4); Ph·NH·NH·Ph, 1·53 (4), 1·66 (5); *p*-$C_6H_4(NH_2)_2$, $<0{\cdot}3$ (6), ~ 0 (7), 0·3 (8), $\sim 1{\cdot}5$ (11), 1·51 (12), 1·56 (9); 1·49 (gas; 10); (*p*-NH$_2$·C_6H_4)$_2$, 1·43 (13), 1·3 (6—8), 1·6 (14); NHPh$_2$, 1·04 (15), 1·08 (16), 1·0 (17), 0·95 (18); NPh$_3$, 0·26 (19), 0·55 (15), 0·47 (18); CHPh$_3$, ~ 0 (liquid; 20), 0·62 (in CS$_2$; 21), 0·21 (22), 0·46 (in dioxan; 22); cyclohexylamine, 1·32 (23).

TABLE 2. *Calculation of results.*

	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *	$10^{12}{}_\infty({}_mK_2)$
Ph·NH·NH$_2$	3·17	0·203	0·063	$2{\cdot}80_5$	$93{\cdot}8_4$	$34{\cdot}7_6$	1·67	16·7
Ph·NH·NH·Ph	2·13	0·237	0·075	$-5{\cdot}41_5$	121·7	59·1	1·70	−80·0
p-NH$_2$·C_6H_4·NH$_2$	2·95	0·255	0·081	−8·95	87·4	34·5	1·58	−79·0
pp'-NH$_2$·C_6H_4·C_6H_4·NH$_2$	2·02	0·280	0·119	−5·73	115·2	63·3	1·54	−85·0
NHPh$_2$	1·12	0·209	0·087	$3{\cdot}00_7$	81·2	57·4	1·01	40·6
NPh$_3$	0·609	0·222	0·110	$1{\cdot}42_4$	93·0	83·2	0·52	33·3
CHPh$_3$ †	0·746	−0·439	0·175	$3{\cdot}64_1$	83·7	$77{\cdot}9_7$	0·3	8·3
Cyclohexylamine	1·86	−0·020	−0·033	1·22	69·1	31·1	1·33	10·6

* Calc., 1·05R_D being taken as the distortion polarisation. † Examined in CCl$_4$.

We confirm the higher polarities ascribed to *p*-phenylenediamine and benzidine by Tiganik [9] and Sutton *et al.*[14] respectively; agreement with literature is otherwise reasonably satisfactory. No determinations of molar Kerr constants antedate those of Tables 1 and 2, although the electric birefringences of one solution in benzene of *p*-phenylenediamine, two of hydrazobenzene, and one of benzidine were included by Lippmann in his 1912 Thesis (see ref. 24); *B* for supercooled phenylhydrazine is listed as zero in the I.C.T., Vol. VII.

DISCUSSION

Bond and group semi-axes of polarisability, now required for discussion, are:

	C–H	N–H	N–C	N–N	" Phenyl "
$10^{23}b_L$	0·064	0·050	0·057	0·062	1·056
$10^{23}b_T$	,,	0·083	0·069	0·077	1·056
$10^{23}b_V$	,,	0·083	0·069	0·077	0·672

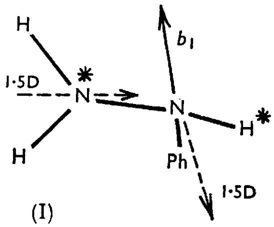
The sources of the first three sets of these are in refs. 1 and 2; the " phenyl " semi-axes come from those ($1{\cdot}12_0$, $1{\cdot}12_0$, and $0{\cdot}73_6$) recalculated from ${}_mK_{\text{benzene}} = 7{\cdot}24 \times 10^{-12}$ and

---

[4] Audrieth, Nespital, and Ulich, *J. Amer. Chem. Soc.*, 1933, **55**, 673.
[5] Cowley and Partington, *J.*, 1933, 1252.
[6] Williams, *Phys. Z.*, 1928, **29**, 683.
[7] Williams and Weissberger, *J. Amer. Chem. Soc.*, 1928, **50**, 2332.
[8] *Idem, Z. phys. Chem.*, 1929, **3**, 367.
[9] Tiganik, *Z. phys. Chem.*, 1931, *B*, **14**, 135.
[10] Linke, *Z. phys. Chem.*, 1940, *B*, **46**, 261.
[11] Fogelberg and Williams, *Phys. Z.*, 1930, **31**, 363.
[12] Bretscher and Wagner-Jauregg, *Helv. Phys. Acta*, 1929, **2**, 522.
[13] Bretscher, *Helv. Phys. Acta*, 1928, **1**, 355.
[14] Everard, Kumar, and Sutton, *J.*, 1951, 2807.
[15] Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1565.
[16] Smith, *J.*, 1950, 3532.
[17] Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1951, **47**, 357.
[18] Cowley, *J.*, 1952, 3558.
[19] Bergmann and Schütz, *Z. phys. Chem.*, 1932, *B*, **19**, 401.
[20] Lautsch, *Z. phys. Chem.*, 1928, *B*, 1, 115.
[21] Bergmann, Engel, and Wolff, *Z. phys. Chem.*, 1932, *B*, **17**, 81.
[22] Syrkin and Shott-L'vova, *Acta Physicochim. U.R.S.S.*, 1944, **19**, 379.
[23] Lewis and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 3067.
[24] Tables Ann. Internat. de Constants et Données Numériques, Vol. II, pp. 355, 356

${}_{\mathrm{E}}P_{\text{benzene}} = 25{\cdot}0_2$ c.c.; the b_{L} for the N–N link has been predicted from $r_{\mathrm{N-N}} = 1{\cdot}45$ Å (cf. dimethylhydrazine in Allen and Sutton's list [25]) by Le Fèvre's equation,[26] and $b_{\mathrm{T}}^{\mathrm{N-N}} = b_{\mathrm{V}}^{\mathrm{N-N}}$ accepted as half of the difference between $b_{\mathrm{L}}^{\mathrm{N-N}}$ and the total polarisability ($0{\cdot}215 \times 10^{-23}$) found by extrapolating the bond refractivities of Vogel *et al.*[27] to $R_{\infty}^{\mathrm{N-N}}$ and multiplying by $9/4\pi N$.

Using these data, we now consider the molecular conformations apparently adopted by each of the solutes named in the following sub-titles.



(I)

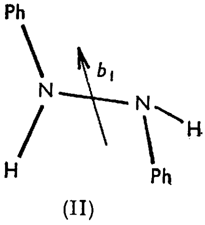
Phenylhydrazine.—The principal axes are based upon those already given for aniline[1] and include the exaltations noted with this molecule in *J.*, 1960, 2161. To provide maximum orbital overlap, the plane of the benzene ring is maintained parallel to a line joining N* and H*. The moment of H–N is 1·3 D (from $\mu_{\mathrm{NH_3}}$); hence the amino-group produces a component of 1·5 D acting at 55° to the N–N longitudinal axis. The unit $\mathrm{N^*{-}N}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{Ph}\end{smallmatrix}$ likewise contributes a component of 1·5 D acting at *ca.* 43° to the C–N direction and in the plane containing b_1 and b_3 of the phenylhydrazine molecule.

Calculations have been made for three conformations: (*a*) in which the plane of N*–N and the bisector of the angle H–N*–H is at right-angles to the plane of N*–N and the bisector of the angle H–N–C, and in which the free electron-pair of the NH_2 group is "*trans*" to the benzenoid ring; (*b*) as (*a*) but with the lone-pair "*cis*" to the benzene ring; and (*c*) in which the nitrogen atoms are twisted about the N–N line so that their four valency directions are anti-parallel. We find (all *b* values × 10^{23}):

$$\text{for } (a)\begin{cases} b_1 = 1{\cdot}65 \\ b_2 = 1{\cdot}29 \\ b_3 = 0{\cdot}96 \end{cases}\!\!\!\left.\vphantom{\begin{cases}1\\1\\1\end{cases}}\right\} \begin{matrix}\mu_{\text{res}},\ \text{calc.} = 1{\cdot}6\ \text{D}, \\ {}_{\mathrm{m}}K,\ \text{calc.} = 5 \times 10^{-12};\end{matrix} \qquad \text{for } (b)\begin{cases} b_1 = 1{\cdot}62 \\ b_2 = 1{\cdot}31 \\ b_3 = 0{\cdot}97 \end{cases}\!\!\!\left.\vphantom{\begin{cases}1\\1\\1\end{cases}}\right\} \begin{matrix}\mu_{\text{res}},\ \text{calc.} = 2{\cdot}9\ \text{D}, \\ {}_{\mathrm{m}}K,\ \text{calc.} = 322 \times 10^{-12};\end{matrix}$$

$$\text{for } (c)\begin{cases} b_1 = 1{\cdot}62 \\ b_2 = 1{\cdot}29 \\ b_3 = 0{\cdot}99 \end{cases}\!\!\!\left.\vphantom{\begin{cases}1\\1\\1\end{cases}}\right\} \begin{matrix}\mu_{\text{res}}\ \text{calc.} = 2{\cdot}6\ \text{D}, \\ {}_{\mathrm{m}}K,\ \text{calc.} = 296 \times 10^{-12}\end{matrix}$$

As the observed moment and molar Kerr constant is $1{\cdot}6_7$ D and $16{\cdot}7 \times 10^{-12}$ respectively, conformation (*a*) is advanced as a near approximation; it has a close relation to the "skew" arrangement postulated by Penney and Sutherland [28] for hydrazine itself.



(II)

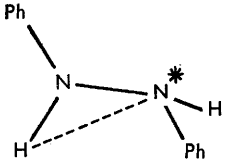
Hydrazobenzene.—Two conformations are considered; in either μ_{res} acts parallel to the minimum polarisability axis b_3. The models may be described by reference to (II). In (*a*) the plane containing N–N and N–H bisects the opposing angle C–N–H, and the benzene rings are "*trans*" to one another and disposed to allow maximum orbital overlap with their respective nitrogen lone-pair orbitals; the largest polarisability semi-axis b_1 is taken as parallel to the N–C longitudinal axis. In model (*b*) the b_1, b_2, and b_3 directions are retained as in (*a*) and each Ph·NH unit is rotated 30° upwards about the N–N axis, so that the two N–H bonds are making their closest approach.

We find (*b* values × 10^{23}):

$$\text{for } (a)\begin{cases} b_1 = 2{\cdot}90 \\ b_2 = 2{\cdot}06 \\ b_3 = 1{\cdot}75 \end{cases}\!\!\!\left.\vphantom{\begin{cases}1\\1\\1\end{cases}}\right\} \begin{matrix}\mu_3 = \mu_{\text{res}} = 1{\cdot}7\ \text{D}, \\ {}_{\mathrm{m}}K,\text{calc.} = -182 \times 10^{-12};\end{matrix} \qquad \text{for } (b)\begin{cases} b_1 = 2{\cdot}61 \\ b_2 = 1{\cdot}97 \\ b_3 = 2{\cdot}14 \end{cases}\!\!\!\left.\vphantom{\begin{cases}1\\1\\1\end{cases}}\right\} \begin{matrix}\mu_3 = \mu_{\text{res}} = 1{\cdot}7\ \text{D}, \\ {}_{\mathrm{m}}K,\text{calc.} = -32 \times 10^{-12};\end{matrix}$$

---

[25] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.
[26] Le Fèvre, *Proc. Chem. Soc.*, 1958, 283.
[27] Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 531.
[28] Penney and Sutherland, *Trans. Faraday Soc.*, 1934, **30**, 898.



(III)

The observed ${}_{\mathrm{m}}K$ (-80×10^{-12}) lies between those expected for (*a*) and (*b*). The structure indicated is therefore intermediate: *e.g.*, one in which the planes bisecting the two C–N–H angles are mutually perpendicular (cf. N_2H_4 and $C_6H_5{\cdot}NH{\cdot}NH_2$). Possibly also each benzene ring does not have its transverse axis exactly parallel to H ··· N- [see (III)] but is twisted away from N*, owing to the greater steric requirement of N* than H. This would increase the contributions of the transverse polarisabilities of the C_6H_5-rings to the molecular b_3, which in consequence would be larger than estimated above for (*a*) and (*b*); ${}_{\mathrm{m}}K$, calc. would, in turn, be less negative.

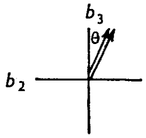
p-*Phenylenediamine.*—We consider first three conformations in which the H ··· H lines of the amino-groups are (*a*) both parallel to the plane of the benzenoid ring and on the same side of it, (*b*) one parallel and one perpendicular to the C_6-plane, and (*c*) both parallel to the C_6-plane but on opposite sides of it. The moment of each amino-group is taken as acting at 50° to the 1,4-line; in aniline the corresponding angle has been thought to be 43°; it would be 55° for a completely tetrahedral non-resonating system.

We predict (values of *b*'s × 10^{23}):

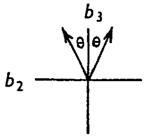
$$\text{for }(a)\left\{\begin{matrix} b_1 = 1{\cdot}418 \\ b_2 = 1{\cdot}367 \\ b_3 = 1{\cdot}046 \end{matrix}\right\} \begin{matrix} \mu_{\mathrm{res}},\text{ calc.} = 2{\cdot}3\text{ D}, \\ {}_{\mathrm{m}}K,\text{ calc.} = \\ -197 \times 10^{-12}; \end{matrix} \qquad \text{for }(b)\left\{\begin{matrix} b_1 = 1{\cdot}418 \\ b_2 = 1{\cdot}396 \\ b_3 = 1{\cdot}016 \end{matrix}\right\} \begin{matrix} \mu_{\mathrm{res}},\text{ calc.} = 1{\cdot}6\text{ D}, \\ {}_{\mathrm{m}}K,\text{ calc.} = \\ -23 \times 10^{-12}; \end{matrix}$$

$$\text{for }(c)\left\{\begin{matrix} b_1 = 1{\cdot}418 \\ b_2 = 1{\cdot}367 \\ b_3 = 1{\cdot}046 \end{matrix}\right\} \begin{matrix} \mu_{\mathrm{res}},\text{ calc.} = 0\text{ D}, \\ {}_{\mathrm{m}}K,\text{ calc.} = +6 \times 10^{-12} \end{matrix}$$

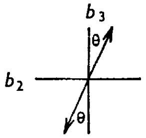
An equimolecular mixture of (*a*) and (*c*) should show $\mu_{\mathrm{res}} = 1{\cdot}6$ D and ${}_{\mathrm{m}}K = -95{\cdot}5 \times 10^{-12}$ (against "found" values of $1{\cdot}5_8$ D and -79×10^{-12}), and an equimolecular mixture of all three forms should show $\mu_{\mathrm{res}} = 1{\cdot}6$ D and ${}_{\mathrm{m}}K = -71 \times 10^{-12}$. Attention has also been given to conformations derived from (*a*) and (*c*) by rotations about the N–Ar bonds of the NH_2 group by various angles θ. The case where θ = 0 has been discussed in (*a*) and (*c*). The directions of action of the resultant moments are indicated by the "end-on" drawings (IV*a*—*d*). The cases where rotation is 20°, 30°, and 45° are considered, the semi-axes (×10^{23}) for the three sets of four isomers being:



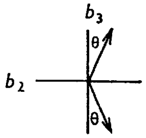
(IV*a*)



(IV*b*)



(IV*c*)



(IV*d*)

$$\text{for }20^{\circ}\left\{\begin{matrix} b_1 = 1{\cdot}42 \\ b_2 = 1{\cdot}38 \\ b_3 = 1{\cdot}03 \end{matrix}\right\} \qquad \text{for }30^{\circ}\left\{\begin{matrix} b_1 = 1{\cdot}42 \\ b_2 = 1{\cdot}38 \\ b_3 = 1{\cdot}03 \end{matrix}\right\} \qquad \text{for }45^{\circ}\left\{\begin{matrix} b_1 = 1{\cdot}42 \\ b_2 = 1{\cdot}40 \\ b_3 = 1{\cdot}02 \end{matrix}\right\}$$

TABLE 3. *Calculated values for* μ_{res} *and* ${}_{\mathrm{m}}K$ *for* p-*phenylenediamine.*

		(IV*a*)	(IV*b*)	(IV*c*)	(IV*d*)
for θ = 20°	μ calc. (D)	2·3	2·1	0	0·8
	$10^{12}{}_{\mathrm{m}}K$, calc.	−170	−181	+7	+17
for θ = 30°	μ, calc. (D)	2·3	2·0	0	1·1
	$10^{12}{}_{\mathrm{m}}K$, calc.	−133	−157	+7	+27
for θ = 45°	μ, calc. (D)	2·3	1·6	0	1·6
	$10^{12}{}_{\mathrm{m}}K$, calc.	−54	−104	+7	+59

Equivalent mixtures of these would lead to moments and molar Kerr constants as follows:

θ	0°	20°	30°	45°
μ_{res} (D)	1·6	1·6	1·6	1·6
$10^{12}\,{}_{\text{m}}K$	−95·5	−82	−64	−23

Accordingly, we conclude that the conformations actually present are those in which NH_2 rotations of *ca.* 20° have occurred.

Benzidine.—With this molecule, rotations of the C_6-rings have to be considered in addition to those of the amino-groups. First, let each NH_2 group be disposed towards its Ar-ring as in conformation (*a*) for *p*-phenylenediamine, and suppose that one half of the molecule rotates around the 4,1,1′,4′-axis; if α is the angle of rotation (such that $\alpha = 0°$ when the C_6-rings are coplanar), then semi-axes, resultant moments, etc., are predicted as follows:

α	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	μ_{res} (D)	$10^{12}\,{}_{\text{m}}K$, calc.	α	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	μ_{res} (D)	$10^{12}\,{}_{\text{m}}K$, calc.
0°	2·503	2·380	1·679	2·3	−417	60°	2·503	2·206	1·853	2·0	−206
30	,,	2·335	1·724	2·2	−347	90	,,	2·030	2·030	1·6	−56
45	,,	2·279	1·780	2·1	−298	180	,,	2·380	1·679	0	+28

The nearest approach to the quantities observed is made when $\alpha = 90°$. However, resonance effects between the two Ar-rings must be expected: they would exalt b_1 (so that the ${}_{\text{m}}K$'s for all but the last form should be more negative than shown above); they would also tend to keep the C_6-rings in one plane. Accordingly, we have performed for benzidine calculations parallel to those made for conformations (IV*a*—*d*) of *p*-phenylenediamine. Results are given in Table 4. Data in parentheses come from the use of the polarisability semi-axes ascribed by Chau, Le Fèvre, and Le Fèvre [29] to the biphenyl molecule itself. Semi-axes calculated for rotations of 30°, 38°, and 45° are:

$$\text{for } 30°\left\{\begin{array}{l}10^{23}b_1 = 2{\cdot}50\ (2{\cdot}7)\\ 10^{23}b_2 = 2{\cdot}39\ (2{\cdot}4)\\ 10^{23}b_3 = 1{\cdot}67\ (1{\cdot}6_4)\end{array}\right\}\quad \text{for } 38°\left\{\begin{array}{l}10^{23}b_1 = 2{\cdot}50\ (2{\cdot}7)\\ 10^{23}b_2 = 2{\cdot}40\ (2{\cdot}4)\\ 10^{23}b_3 = 1{\cdot}66\ (1{\cdot}6_3)\end{array}\right\}\quad \text{for } 45°\left\{\begin{array}{l}10^{23}b_1 = 2{\cdot}50\ (2{\cdot}7)\\ 10^{23}b_2 = 2{\cdot}41\ (2{\cdot}4)\\ 10^{23}b_3 = 1{\cdot}65\ (1{\cdot}6_3)\end{array}\right\}$$

TABLE 4. *Calculated values for* μ_{res} *and* ${}_{\text{m}}K$ *for benzidine.*

		(IV*a*)	(IV*b*)	(IV*c*)	(IV*d*)
for $\theta = 30°$	μ, calc. (D)	2·3	2·0	0	1·1
	$10^{12}\,{}_{\text{m}}K$, calc.	−260 (−312)	−313 (−356)	+29 (+42)	+73 (+77)
for $\theta = 38°$	μ, calc. (D)	2·3	1·8	0	1·4
	$10^{12}\,{}_{\text{m}}K$, calc.	−183 (−239)	−253 (−294)	+30 (+46)	+99 (+100)
for $\theta = 45°$	μ, calc. (D)	2·3	1·6	0	1·6
	$10^{12}\,{}_{\text{m}}K$, calc.	−107 (−156)	−196 (−213)	+31 (+42)	+126 (+112)

Mixtures of equal parts should show dipole moments and molar Kerr constants as follow:

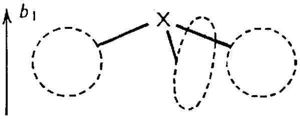
θ	0°	30°	38°	45°
μ_{res} (D)	1·6	1·6	1·6	1·6
$10^{12}\,{}_{\text{m}}K$	−195 (−232)	−118 (−137)	−77 (−97)	−36 (−54)

It is to be noted that a conformation in which the H ·· H directions in the NH_2 groups are one parallel and one perpendicular to the biphenyl plane has the same semi-axes as have the forms represented by $\theta = 45°$; the μ_{res} and ${}_{\text{m}}K$, calc. for this single conformation are numerically the same as those obtained for an equivalent mixture of the preceding four isomers. However, the ${}_{\text{m}}K$ observed is -85×10^{-12} (*i.e.*, more negative than that forecast for either of the cases where the H ··· H lines are mutually perpendicular); accordingly, we conclude that each of the actual conformations present in solution contains a planar biphenyl nucleus with the NH_2 groups rotated so that θ is *ca.* 38°.

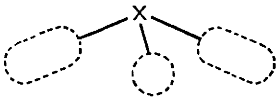
---

[29] Chau, Le Fèvre, and Le Fèvre, *J.*, 1959, 2666.

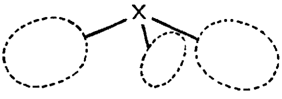
Triphenylamine.—Semi-axes predicted for three conformations are shown beneath (Va, b, and c):



(V*a*); X = N
(VI*a*); X = CH



(V*b*); X = N
(VI*b*); X = CH



(V*c*); X = N
(VI*c*); X = CH

	(V*a*)	(V*b*)	(V*c*)
$10^{23}b_1$ =	3·354	2·283	2·820
$10^{23}b_2$ =	2·770	3·306	3·037
$10^{23}b_3$ =	2·770	3·306	3·037

In (V*a*) the planes of the benzene rings intersect along the line of action of μ_{res}; in (V*b*) and (V*c*) the benzene rings have been rotated about the C–N bonds by 90° and 45° respectively from their dispositions in (V*a*). The angle C–N–C is (following Leonard and Sutton[15]) taken as 114°.

R_∞, computed from R_D = 83·2 c.c. and R_G = 87·5 c.c., is 78·6 c.c., whence $b_1 + 2b_2 = 9{\cdot}34_6 \times 10^{-23}$ (the reasonable assumption being made that the polarisability ellipsoid of this molecule is one of rotation, *i.e.*, with $b_2 = b_3$). From the observed $_{m}K$ and moment, semi-axes are accordingly calculable as $10^{23}b_1 = 2{\cdot}53_7$, $10^{23}b_2 = 3{\cdot}40_5$, or $10^{23}b_1 = 3{\cdot}65_2$, $10^{23}b_2 = 2{\cdot}84_7$. An exaltation in the total polarisability, $b_1 + 2b_2$, of $0{\cdot}45 \times 10^{-23}$ c.c. is thus seen. Since exaltation should be a maximum along the Ph–N directions, which are only 15° from the plane normal to μ_{res}, we select the first set of axes (with $b_2 = b_3 = 3{\cdot}40_5 \times 10^{-23}$) as the more correct. A conformation midway between (V*b*) and (V*c*) [*i.e.*, with the phenyl groups rotated 65—70° from their positions in (V*a*)], or a mixture of these forms, therefore fits the measurements now recorded: with no allowance for exaltation, an equal-part mixture should show $10^{23}b_1 = 2{\cdot}55$ and $10^{23}b_2 = 3{\cdot}17_5$; if the exaltation is added to the $b_2 = b_3$ axes the corresponding values should be $10^{23}b_1 = 2{\cdot}55$ and $10^{23}b_2 = 3{\cdot}40$, in good accord with the result by experiment.

Triphenylmethane.—This molecule was investigated because of its relation to triphenylamine, N^{III} being isoelectronic with CH^{III}. The assumption that the conformation has axial symmetry is again made, so that b_1 is located along the C–H direction, and $b_2 = b_3$ are in a plane normal to the C–H line. From the dispersion data of Kikina, Syrkin, and Shott-L'vova,[30] R_∞ is 77·97 c.c., whence $b_1 + 2b_2 = 9{\cdot}271 \times 10^{-23}$. The observed molar Kerr constant is $8{\cdot}3 \times 10^{-12}$, but the resultant dipole moment is very small and therefore doubtful; semi-axes have therefore been computed with μ = 0·3 D or 0 D:

	with μ_{res} = 0·3 D			with μ_{res} = 0 D		
$10^{23}b_1$	$2{\cdot}73_4$	or	$3{\cdot}30_8$	$2{\cdot}81_2$	or	$3{\cdot}36_8$
$10^{23}b_2 = 10^{23}b_3$	$3{\cdot}26_8$		$2{\cdot}98_2$	$3{\cdot}22_9$		$2{\cdot}95_1$

Using bond and group polarisabilities in conjunction with a Ph–C–Ph angle[15] of 114°, we have calculated semi-axes for three conformations, (VI*a*—*c*) in which the benzene rings are disposed as in (V*a*—*c*) respectively. We obtain

	(VI*a*)	(VI*b*)	(VI*c*)
$10^{23}b_1$	$3{\cdot}31_0$	$2{\cdot}24_2$	$2{\cdot}77_6$
$10^{23}b_2$	$2{\cdot}82_6$	$3{\cdot}35_9$	$3{\cdot}09_3$

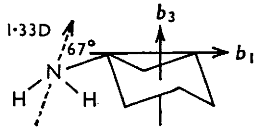
Again an exaltation in $b_1 + 2b_2$ is revealed, and for the same reasons as with triphenylamine it suggests that, of the alternative solutions provided by our experimental data, those in which $b_2 = b_3$ exceeds b_1 are the more correct. Kikina, Syrkin, and Shott-L'vova[30] have drawn attention to the exaltation of molecular refraction exhibited by triphenylmethane, stating this to be much higher than would be expected from purely benzenoid structures. Since inter-ring conjugation appears here to be impossible, presumably the exaltation is to be attributed to hyperconjugation involving the C–H link.

When the exaltation of polarisability is distributed over the semi-axes ($b_2 = b_3$) where it is most likely to occur, we have for conformations (VI*b*) and (VI*c*):

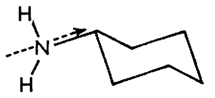
	(VI*b*)	(VI*c*)		(VI*b*)	(VI*c*)
$10^{23}b_1$	2·24	2·78	$10^{23}b_2 = 10^{23}b_3$	3·51	3·24

Comparison of these values with those from experiment indicates that the solute species in carbon tetrachloride resemble (VI*c*) much more than (VI*b*), or alternatively, that if a mixture of forms is present, (VI*c*) is predominant. It is of interest that Rousset and Pacault [31] suggest (from light-scattering measurements) that the benzene rings are rotated *ca.* 60° from the (VI*a*) conformation, while Adrian,[32] from *a priori* calculations of steric energies, has more recently deduced the " equilibrium twist angle " as 50°, in harmony with our value of *ca.* 45°.

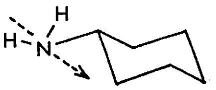
Cyclohexylamine.—We have considered the amino-group to be attached equatorially to a " chair " cyclohexyl conformation, since cyclohexylamine hydrochloride has been reported [33] as " completely chair-equatorial." The bond moment of N–H is 1·3 D (from μ_{NH_3}), so that if the angle H–N–H is 110°, μ_{NH_2} should be 1·5 D acting at 55° to the C–N axis. To obtain a molecular resultant of 1·33 D (the observed value) a component of *ca.* 0·3 D must act along the C→N direction. On combination of these, μ_{res} must act at 67° to the N–C line. Carbon valency angles have been taken throughout as tetrahedral. Polarisability calculations have been made for the three conformations (VII*a*—*c*), in which the centre-centre lines of the amino-hydrogen atoms and the 2,6-carbon atoms are respectively parallel, perpendicular, and parallel to one another. Details and results are shown below:



(VIIa)



(VIIb)



(VIIc)

$$(\text{VII}a)\left\{\begin{array}{l}10^{23}b_1 = 1{\cdot}266\\ 10^{23}b_2 = 1{\cdot}273\\ 10^{23}b_3 = 1{\cdot}104\end{array}\right\}\begin{array}{c}10^{12}{}_{\text{m}}K,\ \text{calc.} =\\ -31\end{array}\qquad (\text{VII}b)\left\{\begin{array}{l}10^{23}b_1 = 1{\cdot}270\\ 10^{23}b_2 = 1{\cdot}243\\ 10^{23}b_3 = 1{\cdot}130\end{array}\right\}\begin{array}{c}10^{12}{}_{\text{m}}K,\ \text{calc.} =\\ +10\end{array}$$

$$(\text{VII}c)\left\{\begin{array}{l}10^{23}b_1 = 1{\cdot}266\\ 10^{23}b_2 = 1{\cdot}273\\ 10^{23}b_3 = 1{\cdot}104\end{array}\right\}10^{12}{}_{\text{m}}K,\ \text{calc.} = -9$$

Conformation (VII*b*) is clearly in best agreement with measurement.

Hydrazine.—Hydrazine hydrate was refluxed over sodium hydroxide pellets for 3 hr. under nitrogen, and the product twice distilled from fresh sodium hydroxide in a current of dry nitrogen; it had b. p. 113°. Solutions in benzene quickly become turbid (access of atmospheric moisture and carbon dioxide during our measurements could not be entirely prevented) and great difficulty was experienced in maintaining the high voltage across the Kerr cell; moreover, the brass electrodes in the cell were visibly attacked and gas bubbles (? nitrogen) were slowly formed. Hydrazine concentrations were found by titration with potassium iodate in acid solution (see Vogel [34]). A number of observations of electric birefringence, taken rapidly before conduction or discharge set in, were ultimately

---

[30] Kikina, Syrkin, and Shott-L'vova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1954, 563.

[31] Rousset and Pacault, *Compt. rend.*, 1954, **338**, 1705.

[32] Adrian, *J. Chem. Phys.*, 1958, **28**, 608.

[33] Sutton, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* No. 11, 1958, M 207.

[34] Vogel, " A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 2nd edn., p. 365.

made, but accurate readings could not be achieved and we can safely report only a small positive effect with respect to benzene solvent for concentrations of *ca.* 0·3%. Such behaviour is not inconsistent with the N–N link's having semi-axes of polarisability: $b_{\mathrm{L}}^{\mathrm{N-N}} = 0{\cdot}062 \times 10^{-23}$, $b_{\mathrm{T}}^{\mathrm{N-N}} = b_{\mathrm{V}}^{\mathrm{N-N}} = 0{\cdot}077 \times 10^{-23}$, as derived at the beginning of this Discussion. The structure of hydrazine on the Penney–Sutherland [28] model is one in which the planes bisecting the H–N–H angles are at right-angles to each other. If bond angles are 110° and the polarisability ellipsoids for N–H as in ref.1 , we have for hydrazine: $b_1 = 0{\cdot}379 \times 10^{-23}$ and $b_2 = b_3 = 0{\cdot}330 \times 10^{-23}$, since $b_1 + 2b_2 = 1{\cdot}040 \times 10^{-23}$ (calc.[27] from $R_{\mathrm{D}}^{\mathrm{N_2H_4}} = 9{\cdot}03$ and $R_{\mathrm{G}}^{\mathrm{N_2H_4}} = 9{\cdot}28$ c.c.). The dipole moment [4] in benzene is 1·84 D. Accordingly, ${}_{\mathrm{m}}K$, calc. should be $-9{\cdot}0 \times 10^{-12}$. From ref. 4 we compute $\alpha\varepsilon_1 = 12{\cdot}9$, $\beta = 0{\cdot}66$, and $\gamma = 0{\cdot}20$. The value of $\Delta B/w_2$ required to give ${}_{\mathrm{m}}K = -9{\cdot}0 \times 10^{-12}$ is $+0{\cdot}90$ which, for solutions of w_2 near 0·003, would correspond to a ΔB of $+0{\cdot}003 \times 10^{-7}$.

We acknowledge with gratitude a gift of pure triphenylmethane from Miss J. Bosson.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, December 7th,* 1959.]