10. *Studies in Dielectric Polarisation. Part XIV. The Dipole Moments of Ethyl, Phenyl, and α- and β-Naphthyl* iso*Cyanates.*

By ERIC G. COWLEY and JAMES R. PARTINGTON.

PART IV of this series (J., 1932, 2825) recorded the dipole moments of the alkyl *iso*thiocyanates measured in benzene solution; it was found that a linear structure satisfactorily accounted for the magnitude of the moments, and the Raman spectra of these compounds (Langseth, Nielsen, and Sørensen, *Z. physikal. Chem.*, 1934, *B*, **27**, 100) have confirmed this conclusion. The work has now been extended to the *iso*cyanates, for which, again, a linear structure is indicated (Cowley and Partington, *Nature*, 1935, **135**, 1038). The present paper describes the moments of ethyl, phenyl, and α- and β-naphthyl *iso*cyanates, the values found in benzene being 2·81, 2·28, 2·30, and 2·34 respectively (Debye units are used throughout). The moment of phenyl *iso*cyanate had previously been found to be 2·23 at 25° in benzene (Sidgwick, Sutton, and Thomas, J., 1933, 406) and 2·34 at 18° in carbon tetrachloride (Eide and Hassel, *Tidsskr. Kjemi Berg.*, 1930, **10**, 93), but no data are available for the other compounds.

Phenyl and α-naphthyl *iso*cyanates have approximately the same moment, that of β-naphthyl *iso*cyanate being somewhat greater. These results are similar to those for the corresponding halogen compounds, as is shown by the following values for the moments determined in benzene: chlorobenzene 1·56 (Smyth, Morgan, and Boyce, *J. Amer. Chem. Soc.*, 1928, **50**, 1536); α-chloronaphthalene 1·59 (Parts, *Z. physikal. Chem.*, 1930, *B*, **10**, 264), 1·50 (Nakata, *Ber.*, 1931, **64**, 2059); β-chloronaphthalene 1·72 (Parts, *loc. cit.*), 1·57 (Nakata, *loc. cit.*). The values (in benzene) for phenol and α- and β-naphthol, *viz.*, 1·73 (Smyth and Morgan, *J. Amer. Chem. Soc.*, 1927, **49**, 1030), 1·0, and 1·3 (Puchalik, *Physikal. Z.*, 1932, **33**, 341) respectively, show a different behaviour.

The moment of the *iso*cyanate group is greater in the aliphatic than in the aromatic series, and this is parallel to the behaviour of the *iso*thiocyanate group. In both groups the resultant moment acts in the same sense, the oxygen or the sulphur atom being at the negative end of the dipole, since the sign of the moment is the same as that of the C–Cl dipole.

The dipole moments of the *iso*thiocyanates are larger than those of the *iso*cyanates, owing to the fact that the C=S is greater than the C=O moment; this excess is shown below for corresponding members of the two series, the solvent being benzene in every case:

Ethyl *iso*thiocyanate	3·31 [1]	Phenyl *iso*thiocyanate	3·00 [3]	2·76 [3a]
Ethyl *iso*cyanate	2·81 [2]	Phenyl *iso*cyanate	2·28 [2]	
Difference	0·50	Difference	0·72	0·48
Thiobenzophenone	3·37 [4]	Dianisyl thioketone	4·44 [5]	
Benzophenone	2·95 [6]	Dianisyl ketone	3·90 [5]	
Difference	0·42	Difference	0·54	

---

[1] Hunter and Partington, J., 1932, 2825.

[2] Present research.

[3] Bergmann and Tschudnowsky, *Z. physikal. Chem.*, 1932, *B*, **17**, 100; [3a] Bergmann, Engel, and Sandor, *ibid.*, 1930, *B*, **10**, 397.

[4] Hunter and Partington, J., 1933, 87.

[5] Donle and Volkert, *Z. physikal. Chem.*, 1930, *B*, **8**, 60 (both moments corrected for P_A).

[6] Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446.

The linear structure of the *iso*thiocyanates (see above) is in agreement with the fact that the moment shows an increase from the methyl to the ethyl compound. The nitrogen atom in the *iso*thiocyanates and *iso*cyanates is similarly linked, so that it is probable that the configuration of the valency bonds will be the same in the two groups. In both series the approximate additivity of the group moments in the *p*-substituted *iso*thiocyanates (Bergmann and Tschudnowsky, *loc. cit.*) and *iso*cyanates (Sidgwick, Sutton, and Thomas, *loc. cit.*) is in agreement with the linear structure of the groups. In Part IV (*loc. cit.*), an approximate value of the moment of ethyl *iso*thiocyanate was calculated, and a similar method has been applied to the *iso*cyanates and *iso*thiocyanates by Sutton (*Trans. Faraday Soc.*, 1934, **30**, 789). It has been concluded (Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293; Sutton, *loc. cit.*), from a consideration of the interatomic distances, that resonance probably occurs in the *iso*cyanate group. Of two possible structures, (I) and (II), for these com-

$$\mathrm{R{-}N{=}C{=}X} \qquad \mathrm{R{-}N{\equiv}C{\rightarrow}X} \qquad \mathrm{R{-}N{\leftarrow}C{\equiv}X}$$

(I.) (II.) (III.)

pounds, (I) is excluded since it would not be linear. As, however, a molecule of the type (II) would have a large moment (> 6) whereas the observed moments are in approximate agreement with those calculated for the ordinary structure (I) alone, there must also be resonance with third form (III), which would be present in a quantity equal to that of form (II) to counterbalance the moment of the latter. This conclusion is supported by the values of the energy of these molecules (Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606). The absorption spectra of these compounds have been studied by Sho-Chow Woo and Ta-Kong Liu (*ibid.*, 1935, **3**, 544), who find that the *iso*cyanates are probably represented by (I), in spite of the fact that the characteristic absorption of the keto-group is absent.

Goubeau (*Ber.*, 1935, **68**, 912) now finds that the Raman spectra indicate that the $\mathrm{N{=}C{=}O}$ group in the *iso*cyanic esters is linear, and this conclusion is fully supported by the values of the dipole moments.

EXPERIMENTAL.

Apparatus.—The apparatus and experimental method are identical with those previously described (Cowley and Partington, J., 1935, 604).

Materials.—Kahlbaum's "thiophen-free" benzene, which had been dried by sodium and fractionated, was used as solvent.

Ethyl *iso*cyanate was prepared by heating potassium cyanate with potassium ethylsulphate. The product was fractionated to remove cyanurate, dried with anhydrous sodium sulphate, and twice fractionated. Owing to the instability of this substance, the measurements were made immediately. Methyl *iso*cyanate could not be obtained sufficiently pure for measurement. Phenyl *iso*cyanate (Kahlbaum) was dried and fractionated. The naphthyl *iso*cyanates were obtained from Fraenkel and Landau, Berlin. Great care was taken to avoid contact of the substances with air, as they are easily decomposed by moisture. The physical constants of the specimens were :

Compound.	B. p.	$D_{4^\circ}^{20^\circ}$.	$n_{\mathrm{D}}^{20^\circ}$.
Ethyl *iso*cyanate	59·8°/759 mm.	0·9031	1·3808
Phenyl *iso*cyanate	161·7/752 mm.	1·0946	1·5363
α-Naphthyl *iso*cyanate	267·0/761 mm.	1·1774	—
β-Naphthyl *iso*cyanate	(m. p.) 56·4°	—	—

These figures may be compared with the following previous determinations upon *iso*cyanates : Phenyl, $D_{4^\circ}^{19\cdot6^\circ}$ 1·0956, $n_{\mathrm{D}}^{19\cdot6^\circ}$ 1·5368 (Brühl, *Z. physikal. Chem.*, 1895, **16**, 216), b. p. 162° (Sidgwick, Sutton, and Thomas, *loc. cit.*); α-naphthyl, b. p. 269—270° (Hofmann, *Ber.*, 1870, **3**, 658); β-naphthyl, m. p. 55—56° (Vittenet, *Bull. Soc. chim.*, 1899, **21**, 958).

Results.—Solvent, benzene. All measurements at 20°.

Ethyl *iso*cyanate.

f_2.	ε.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·280	0·8789	26·57	—
0·007563	2·364	0·8790	27·74	181·3
0·026562	2·575	0·8794	30·49	174·1
0·034291	2·660	0·8795	31·52	170·9
0·043812	2·770	0·8798	32·80	168·8
0·050951	2·846	0·8799	33·64	165·3

$P_{2\infty}$ = 185·0 c.c.; P_E = 18·3 c.c.;
$P_{2\infty} - P_E$ = 166·9 c.c.; μ = 2·81.

Phenyl *iso*cyanate.

f_2.	ε.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·280	0·8789	26·57	—
0·009412	2·351	0·8812	27·65	141·3
0·018163	2·418	0·8833	28·64	140·5
0·029040	2·500	0·8861	29·82	138·5
0·043582	2·607	0·8896	31·32	135·6
0·051078	2·667	0·8917	32·04	133·7

$P_{2\infty}$ = 144·0 c.c.; P_E = 33·9 c.c.;
$P_{2\infty} - P_E$ = 110·1 c.c.; μ = 2·28.

α-Naphthyl *iso*cyanate.

f_2.	ε.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·279	0·8788	26·56	—
0·006963	2·336	0·8821	27·49	160·2
0·008945	2·352	0·8829	27·76	160·7
0·025254	2·485	0·8906	29·88	158·0
0·029829	2·522	0·8930	30·45	157·0

$P_{2\infty}$ = 161·5 c.c.; P_E = 49·3 c.c.;
$P_{2\infty} - P_E$ = 112·2 c.c.; μ = 2·30.

β-Naphthyl *iso*cyanate.

f_2.	ε.	$D_{4°}^{20°}$.	P_{12}.	P_2.
0	2·279	0·8788	26·56	—
0·005664	2·327	0·8816	27·34	164·3
0·014629	2·402	0·8860	28·54	161·9
0·015443	2·409	0·8865	28·65	161·9
0·026259	2·499	0·8917	30·07	160·2

$P_{2\infty}$ = 165·5 c.c.; P_E = 49·3 c.c.;
$P_{2\infty} - P_E$ = 116·2 c.c.; μ = 2·34.

SUMMARY.

The dipole moments in Debye units of ethyl (2·81), phenyl (2·28), α-naphthyl (2·30), and β-naphthyl (2·34) *iso*cyanates, measured in benzene solution at 20°, are in agreement with a linear structure for the *iso*cyanate group. It is pointed out that this conclusion is supported by the Raman spectra of these compounds. It is shown that the *iso*cyanate and the *iso*thiocyanate group are similar in configuration.

QUEEN MARY COLLEGE, LONDON, E. 1.

[*Received, October 22nd,* 1935.]