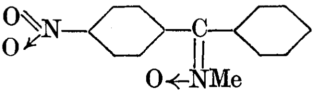
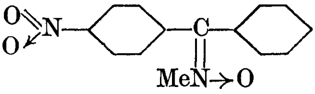
CCXCVII.—*The Configurations of Oximes, from Measurements of Electric Dipole Moment.*

By Leslie Ernest Sutton and Thomas Weston Johns Taylor.

It is of obvious advantage to apply the measurement of the physical properties of isomeric oximes to the elucidation of their stereochemical configurations, as well as to deduce these configurations from their behaviour in chemical reactions. Of such measurements, the electric dipole moment can be used to give a direct and unambiguous indication of stereochemical configuration, as is instanced by the large difference between the moments of the *cis-* and *trans-*forms of dichloroethylene (1·85 and 0×10^{-18} e.s.u., respectively; see Errera, *Compt. rend.*, 1926, **182**, 1623).

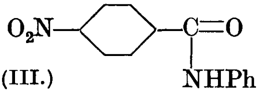
The oximes themselves are largely associated in solution, and this renders them unsuitable for measurements (Hassel and Naeshagen, *Z. physikal. Chem.*, 1929, *B*, 4, 217). Their *N*-ethers, however, do not associate, and the grouping $N\rightarrow O$ which they contain will, by analogy with the nitro-group (nitrobenzene, $\mu = 3{\cdot}9 \times 10^{-18}$ e.s.u.), possess a large moment with the positive pole nearer the nitrogen atom. The method used was to obtain the dipole moments of the *N*-methyl ethers of the two isomeric oximes of *p*-nitrobenzophenone. In these molecules there are two groups possessing large moments, the nitro-group and the *N*-ether group: in one ether (I) the moment should be large, the two groups which are the chief contributors being *cis-* to one another (compare *o*-dinitrobenzene, $\mu = 6{\cdot}02 \times 10^{-18}$ e.s.u.), while in the other (II) the


(I.)

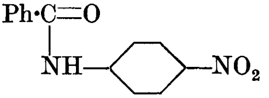

(II.)

moments of these groups will tend to neutralise one another and the resultant moment will be small.

The two isomeric oximes and the *O*- and *N*-ethers derived from them have been obtained. Previous work on their preparation has been recorded by Brady and Mehta (J., 1924, **125**, 2297). According to our results these authors obtained one oxime in the pure state, but the substance which they describe as the second oxime is a mixture of the two. Both oximes can be methylated without any conversion into the other form taking place, and the hypotheses of Brady and Mehta to account for the formation of two *N*-ethers from one of the oximes are therefore unnecessary. Further, both oximes give a single product as the result of the Beckmann transformation. These facts make it possible to deduce the configurations of the oximes themselves from the measurements of dipole moment, and to ascertain which groups are involved in the Beckmann transformation without any ambiguity. The results obtained were as follows. The oxime, m. p. 159°, which will be referred to as the α-oxime, gives an *N*-methyl ether, whose dipole moment is $6{\cdot}60 \times 10^{-18}$ e.s.u., whereas the β-oxime, m. p. 136°, gives an *N*-methyl ether of moment $1{\cdot}09 \times 10^{-18}$ e.s.u. Hence there is little doubt that the α-ether has the stereochemical configuration shown in (I), and the β-ether that shown in (II), and that the former oxime is the *syn*-, and the latter the *anti*-oxime. Brady and Mehta (*loc. cit.*) have shown that the α-oxime gives by the Beckmann rearrangement *p*-nitrobenzanilide (III), and we have found that the β-oxime gives exclusively benzo-*p*-nitroanilide (IV). It is thus established that in this case the groups involved in the Beckmann transformation are those in the *anti*-position to one another, in agreement with the modern interpretation of that transformation.



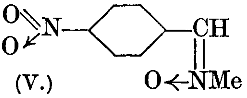
(III.)



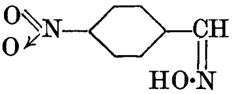
(IV.)

In the case of the aldoximes, the method cannot be applied in so satisfactory a way, because in no case are the two isomeric *N*-ethers of an aldoxime known (Brady, Dunn, and Goldstein, J., 1926, 2386). There is, however, a presumption that the one *N*-methyl ether has the same stereochemical configuration as the β-aldoxime. The evidence for this is not strong; but the yields quoted by Brady, Dunn, and Goldstein (*loc. cit.*) seem to indicate that on methylation under comparable conditions a β-aldoxime gives much larger yields of the *N*-ether than does an α-aldoxime.

The *N*-methyl ether derived from the *p*-nitrobenzaldoxime has been prepared. Its properties (see p. 2193) render the measurement of its dipole moment difficult; but it has been established that its moment is $6{\cdot}4 \pm 0{\cdot}1 \times 10^{-18}$ e.s.u.; the configuration of this ether must therefore be similar to that of the *N*-ether of *syn*-*p*-nitrobenzophenoneoxime (I), and must be (V).



(V.)



(VI.)

The *N*-methyl ethers of aldoximes undergo a Beckmann transformation on heating with acetic anhydride (Brady and Dunn, J., 1926, 2411). Since these authors have shown that *N*-methyl-*p*-nitrobenzaldoxime gives *p*-nitrobenzomethylamide, it is established that in this case also the Beckmann transformation has involved the groups in the *anti*-position to one another. If, further, it be assumed that the *N*-ether is stereochemically related to the β-oxime, the latter must have the analogous configuration (VI). This is in agreement with the modern views on the configurations of aldoximes (von Auwers and Ottens, *Ber.*, 1924, **57**, 446; Brady and Bishop, J., 1925, **127**, 1357; Brady, this vol., p. 105).

EXPERIMENTAL.

Preparation and Purification of Materials.—Oximes of p-*nitrobenzophenone.* *p*-Nitrobenzophenone (Schroeter, *Ber.*, 1909, **42**, 3360) could be purified most easily by recrystallisation from acetone. The mixture of its two oximes was obtained and separated into two main fractions as described by Brady and Mehta (*loc. cit.*). The α-oxime, which forms the sparingly soluble sodium salt, gave after recrystallisation from benzene very pale yellow needles, m. p. 159°, in agreement with the results of these authors. The fraction which forms the more soluble sodium salt was recovered, and on recrystallisation from alcohol and then twice from benzene gave a colourless oxime (β-) melting sharply at 136° (Found: N, 11·6. Calc. for $C_{13}H_{10}O_3N_2$: N, 11·6%). Contrary to the statement of Brady and Mehta, this substance does not consist essentially of the α-oxime: a mixture of it with the α-oxime melts over a range of temperature, beginning at 116°. That this substance is the second (β-) oxime, in a pure state, is shown by the facts (i) that on methylation it gives only one *N*-methyl ether, which is different from that of the α-oxime, and (ii) that, when it undergoes the Beckmann transformation, it gives a single product and not a mixture. The second oxime of Brady and Mehta, which they describe as a buff-coloured powder, m. p. 115°, is clearly a eutectic mixture of the two oximes; they state that on methylation it gave a mixture of two *N*-methyl ethers, and after the Beckmann transformation a mixture of two amides. These buff-coloured mixtures can be obtained from the mother-liquors from the recrystallisation of either crude oxime, and cannot be separated into fractions by repeated recrystallisation.

In the oximation of the ketone (70 g.), approximately equal amounts of the two oximes are formed, about 17 g. of each being obtained in a pure state. There was no sign of interconversion of the oximes at any stage. The α-oxime decomposes on keeping in a corked tube, as is described by Brady and Mehta, but the β-oxime is considerably more stable.

The Beckmann Transformation of the β-*Oxime.*—Treatment of the oxime in ethereal solution with phosphorus pentachloride in the cold, followed by addition to water and removal of the solid, gave a solid, m. p. 179—185°, which, after one recrystallisation from alcohol, melted sharply at 199°. This was shown to be pure benzo-*p*-nitroanilide by a mixed m. p. with a sample obtained from benzoyl chloride and *p*-nitroaniline.

Preparation of the Methyl Ethers of the Oximes.—The α-oxime was methylated according to the method of Brady and Mehta, and these authors' descriptions of the *O*- and the *N*-ether were confirmed.

The β-oxime was methylated in the same way. The crude product was extracted with warm ether, and from the solution the second *O*-methyl ether was obtained; after recrystallisation from methyl alcohol, it formed white shining plates, m. p. 96°. The residue from the ether extraction gave the β-N-*methyl ether* as yellow needles from alcohol, m. p. 186° (Found: N, 10·6. $C_{14}H_{12}O_3N_2$ requires N, 10·9%). There was no sign of the formation of two *N*-ethers. Brady and Mehta, by the methylation of their second oxime, obtained an *O*-ether identical with ours, and a mixture of *N*-ethers from which they separated yellow needles melting at 176°; this is clearly the *N*-ether of the β-oxime largely contaminated with that of the α-oxime. One point, however, remains obscure; these authors state that only one *O*-ether was formed, and from their description it appears to be identical with ours, whereas it would have been expected that, since they were dealing with a mixture of oximes, both the *O*-ethers would have been formed. The hypothesis that the two *O*-ethers form solid solutions would explain their results, but is excluded by the fact that we find mixtures of the two *O*-ethers to melt over the range 76—85°.

N-Methyl-*p*-nitrobenzaldoxime was obtained by the method given by Brady, Dunn, and Goldstein (*loc. cit.*, p. 2401). It was recrystallised three times from benzene, in which it is very sparingly soluble; it is insoluble in the cold in carbon tetrachloride, carbon disulphide, and dioxin.

Measurements of Electric Dipole Moment.—These were measured in benzene solution at 25° by the method used before (Hammick, New, Sidgwick, and Sutton, J., 1930, 1876) with an apparatus and technique to be described elsewhere (*Proc. Roy. Soc.*, 1931, in the press).

The results obtained are tabulated below, where f_2 is the molar fraction of the solute, *d* the density of the solution (those by interpolation marked *), *e* its dielectric constant, *n* its refractive index, P_2 the total polarisation of the solute and ${}_eP_2$ its electron polarisation (Hg-green line, 5461) at 25°.

p-*Nitrobenzophenone-α-oxime* N-*methyl ether.*

f_2.	*d*.	*e*.	*n*.	P_2.	${}_eP_2$.
0·00863	0·8818	2·8121	1·50618	879·3	78·45
0·00604	0·8795	2·6520	1·50498	906·5	79·1
0·00421	0·8775	2·5393		932·9	
0·002896	0·8764*	2·4563		944·9	

P_2 at infinite dilution $= 982$; ${}_eP_2 = 79$ cm.³; $P_2 - {}_eP_2 = 903$ cm.³; $\mu = 6{\cdot}60 \times 10^{-18}$ e.s.u.

p-*Nitrobenzophenone-β-oxime* N-*methyl ether.*

f_2.	*d*.	*e*.	*n*.	P_2.	${}_eP_2$.
0·00563	0·8796	2·2916	1·50458	100·7	75·08
0·004085	0·8779	2·2864	1·50385	99·6	75·63
0·00277	0·8765*	2·2823		99·9	

P_2 at infinite dilution $= 100$; ${}_eP_2 = 75{\cdot}35$ cm.³; $P_2 - {}_eP_2 = 24{\cdot}65$ cm.³; $\mu = 1{\cdot}09 \times 10^{-18}$ e.s.u.

p-*Nitrobenzaldoxime* N-*methyl ether.*

f_2.	*d*.	*e*.	*n*.	P_2.	${}_eP_2$.
0·000376	0·87394	2·2967		900·4	

P_2 at infinite dilution $= 900{\cdot}4$ cm.³.

The difference between ${}_eP_{\mathrm{Hg}\,5461}$ for benzophenone and benzaldehyde is 25·26 (interpolated from ${}_eP_{\mathrm{H}\alpha}$ and ${}_eP_{\mathrm{H}\beta}$, Landolt–Börnstein, "Physikalisch-Chemische Tabellen"). Now ${}_eP_2$ for *p*-nitrobenzophenone-α-oxime *N*-methyl ether is 78·8, hence ${}_eP_2$ for *p*-nitrobenzaldoxime *N*-methyl ether is 53·5 cm.³. Therefore $P_2 - {}_eP_2 = 847$; $\mu = 6{\cdot}4 \times 10^{-18}$ e.s.u.

Owing to the very sparing solubility of this substance in non-polar solvents, the total polarisation could only be measured at one concentration, and the electron polarisation had to be estimated indirectly, as above. If it be assumed that the errors were ± 0·0001 in *d* and ± 0·0002 in *e*, the error in the total polarisation would be ± 3%, *i.e.*, about ± 27 cm.³. The error in the electron polarisation is probably less than 1 cm.³ and is therefore negligible. The error in the value for the moment is thus ± 1·5% (since $\mu \propto \sqrt{P}$), *i.e.*, $\pm\, 0{\cdot}1 \times 10^{-18}$ e.s.u., and although this is comparatively large, the order of the moment is established beyond any doubt.

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