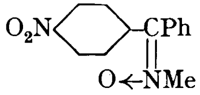
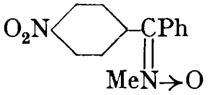
20. *The Configurations of the Aldoximes, from Measurements of Electric Dipole Moment.*

By T. W. J. TAYLOR and L. E. SUTTON.

IN an earlier paper (Sutton and Taylor, J., 1931, 2190) measurements were recorded of the molecular electric dipole moments of the *N*-methyl ethers of the two geometrically isomeric *p*-nitrobenzophenoneoximes, and it was pointed out that the large and very striking difference between the values obtained (α-ether, $\mu = 6{\cdot}60 \times 10^{-18}$ e.s.u., β-ether, $\mu = 1{\cdot}09 \times 10^{-18}$ e.s.u.) could only be accounted for by assigning the configuration (I) to the α-ether and (II) to the isomeric β-ether.

(I.)



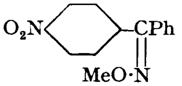
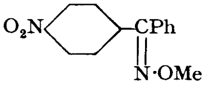
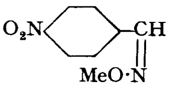
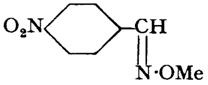


(II.)

Since, in this case, each oxime gives only one *O*-ether and one *N*-ether on methylation, from this result it was possible to assign structures to the oximes themselves and to ascertain the groups which participate in the Beckmann transformation of the oximes. The conclusion so reached as to the configuration of ketoximes in general agrees with those drawn from all other recent work on this subject (see, *inter alia*, Meisenheimer, Theilacker, and Beisswenger, *Annalen*, 1932, **495**, 249) and the total mass of the evidence is so great that it would seem that the configuration of the ketoximes is now settled quite definitely.

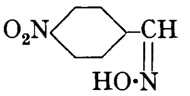
The configurations of the geometrically isomeric aldoximes are not, however, known with any such certainty (for a short discussion of the evidence see Taylor, Winckles, and Marks, J., 1931, 2778). With these oximes a direct appeal to the values of the electric moments of the *N*-ethers is impossible, because in no case are the two isomeric *N*-ethers of an aldoxime known, and there is no method of establishing unambiguously to which of the two aldoximes the one known *N*-ether is related in configuration. The two isomeric *O*-ethers derived from an aldoxime can, however, be obtained, and since, unlike the oximes themselves, they are not associated in solution, their electric moments can be measured. These, by themselves, however, do not enable us to determine the configurations, for, owing to our lack of knowledge of the moments of the component covalencies, and of the complicating effect of rotation of the methyl group about the N–O axis, it is impossible to predict *a priori* which should have the larger moment. Since, however, we can take the configurations of the ketoximes as firmly established, we know the configurations of the *O*-methyl ethers of the ketoximes, if we assume that *O*-methylation does not change the configuration (evidence for the truth of this assumption is mentioned below) and then, by comparing the electric dipole moments of a pair of isomeric *O*-methyl ketoximes with those of the pair of related *O*-methyl aldoximes, we can obtain very clear evidence as to the configurations of the aldoximes themselves.

TABLE I.

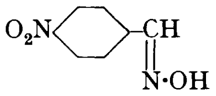
			$\mu \times 10^{18}$.
(III.)		α-*O*-Methyl-*p*-nitrobenzophenoneoxime	$3{\cdot}75$
(IV.)		β-*O*-Methyl-*p*-nitrobenzophenoneoxime	$4{\cdot}26$
		Difference	$0{\cdot}51$
(V.)		β-*O*-Methyl-*p*-nitrobenzaldoxime	$3{\cdot}39_5$
(VI.)		α-*O*-Methyl-*p*-nitrobenzaldoxime	$3{\cdot}88_5$
		Difference	$0{\cdot}49$

The substances investigated were the *O*-methyl ethers of the *p*-nitrobenzophenone oximes and of the *p*-nitrobenzaldoximes; the results obtained and the argument used are shown in Table I.

The configurations of (III) and (IV) are taken as known. Their electric dipole moments differ by 0·51 × 10^{-18} e.s.u. In the closely related aldoxime derivatives, (V) and (VI), which differ only in the substitution of a phenyl group by a hydrogen atom, the moments show the same difference, within the limits of experimental error. Hence it is difficult to avoid the conclusion that the aldoxime and ketoxime derivatives with the smaller moments have a similar configuration, and those with the larger moments the opposite configuration. Thus, the configurations of the aldoxime derivatives must be those shown in (V) and (VI). Again, it being assumed that there is no change of configuration on methylation, this leads to the conclusion that the configurations of the *p*-nitrobenzaldoximes are those shown in (VII) and (VIII), and since the β-oxime is that one whose acetyl derivative loses acetic acid under the action of sodium carbonate, the further conclusion is reached that this loss involves groups in the *anti*-position to one another, and that the original configurations allotted by Hantzsch and Werner must be reversed. Since this result agrees with all the other available evidence on the subject, it may be concluded that the question of the configurations of the aldoximes is settled beyond reasonable doubt.



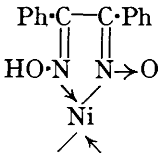
(VII.) *β-p*-Nitrobenzaldoxime

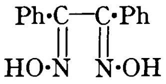


(VIII.) *α-p*-Nitrobenzaldoxime

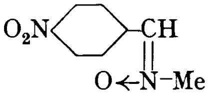
Evidence that there is no change of configuration when an oxime is methylated is afforded by the work of Brady and Muers (J., 1930, 216, 1599) on the properties of the methyl ethers of the benzildioximes. It is now well established that in the nickel derivative, R_2Ni, of α-benzildioxime the attachment of the dioxime residue to nickel is as shown in IX (Hieber and Leutert, *Ber.*, 1929, **62**, 1839), and that such a derivative is formed by the α-dioxime and not by the β-isomeride because the former has the structure (X), in which the space arrangement is already suitable for such attachment to take place.

(IX.)





(X.)



(XI.)

Now Brady and Muers found that mono-*O*-methylation of α-benzildioxime gave an ether which is still capable of forming the complexes R_2Ni and R_3Co. Hence it seems clear that the configuration of the *O*-ether corresponds to that of the parent oxime. It must be emphasised, however, that if the unlikely assumption is made that *O*-methylation always causes reversal of configuration, then the conclusions of this paper are unaffected, since the reversal will have taken place with both the ketoximes and the aldoximes. It is only on the still less likely assumption that methylation has reversed the configuration in the ketoximes and not in the aldoximes, or *vice versa*, that there can be any uncertainty.

Finally, it should be pointed out that the differences in moment which form the basis of the argument, though small, can be measured with ample accuracy because the molecules contain a nitro-group of large moment and thus the total polarisation is large (see Experimental). Further the differences can hardly be affected by uncertainty as to atom polarisation because the molecules in each pair are of precisely the same chemical type and complexity.

The results obtained establish a further point, the relationship of the one *N*-methyl ether which can be obtained from a pair of isomeric aldoximes. In the former paper it was recorded that *N*-methyl-*p*-nitrobenzaldoxime has an electric moment of 6·4 × 10^{-18} e.s.u., and thus must have the configuration (XI); it thus follows that the *N*-ether is related in configuration to the β-aldoxime, as has been suspected previously.

EXPERIMENTAL.

The *O*-methyl-*p*-nitrobenzophenoneoximes were obtained as described in the earlier paper, α-*O*-methyl-*p*-nitrobenzaldoxime by the method of Brady, Dunn, and Goldstein (J., 1926, 2398) and the isomeric β-ether by the action of MeI on the Na salt of the β-oxime (Brady and Dunn, J., **1913**, **103**, 1625).

The samples used for the measurements were recrystallised four times; the observed m. p.'s were : α-*O*-methyl-*p*-nitrobenzophenoneoxime 93° (from MeOH), β-isomeride 96° (from MeOH); α-*O*-methyl-*p*-nitrobenzaldoxime 105° (from C_6H_6), β-isomeride 70° (from acetone + H_2O).

The dipole moment measurements were made with the apparatus and technique described by Sutton (*Proc. Roy. Soc.*, 1931, [*A*], **133**, 668) in C_6H_6 solution at 25°. In the following tables the symbols are those used in the previous paper, with the addition of P_{A+O} for the sum of the atom and orientation polarisations, *i.e.*, the difference $P_2 - {}_eP_2$.

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

f_2.	$d_{4°}^{25°}$.	*e.*	*n.*	P_2.	${}_eP_2$.
0·0108	0·8829	2·4957	1·50531	352	73·7
0·0076	0·8802	2·4309	1·50427	354·5	72·7
0·00524	0·8782	2·3811	—	359	—

P_2 at infinite dilution $= 365 \pm 2$; ${}_eP_2 = 73{\cdot}2 \pm 0{\cdot}5$; $P_{A+O} = 292 \pm 2{\cdot}5$; $\mu = 3{\cdot}75 \pm 0{\cdot}02 \times 10^{18}$ e.s.u.

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

0·0164	0·8874	2·7107	1·50710	424	74·3
0·0122	0·8838	2·6005	1·50596	431·5	74·0
0·0084	0·8807	2·4980	1·50477	437	74·9

P_2 at infinite dilution $= 451 \pm 2$; ${}_eP_2 = 74{\cdot}4 \pm 0{\cdot}5$; $P_{A+O} = 376{\cdot}6 \pm 2{\cdot}5$; $\mu = 4{\cdot}26 \pm 0{\cdot}02 \times 10^{-18}$ e.s.u.

p-*Nitrobenzaldoxime α-*O*-methyl ether.*

0·02175	0·8864	2·7498	1·50573	336	50·3
0·01663	0·8834	2·6375	1·50478	342	50·1
0·0115	0·8804	2·5251	1·50401	348	50·3
0·0079	0·8783*	2·4452	—	350	—

P_2 at infinite dilution $= 363 \pm 2$; ${}_eP_2 = 50{\cdot}2 \pm 0{\cdot}1$; $P_{A+O} = 313 \pm 2$; $\mu = 3{\cdot}88_5 \pm 0{\cdot}01 \times 10^{-18}$ e.s.u.

p-*Nitrobenzaldoxime β-*O*-methyl ether.*

0·0208	0·8862	2·6256	1·50542	275	49·5
0·0155	0·8830	2·5357	1·50437	278	48·9
0·0108	0·8801	2·4560	1·50363	281	49·1
0·0076	0·8782*	2·4016	—	283	—

P_2 at infinite dilution $= 288 \pm 1$; ${}_eP_2 = 49{\cdot}2 \pm 0{\cdot}5$; $P_{A+O} = 239 \pm 1{\cdot}5$; $\mu = 3{\cdot}39_5 \pm 0{\cdot}01 \times 10^{-18}$ e.s.u.

* Taken from the density–molar fraction graph.

The refractivities of the isomeric ethers differ by small amounts; the sense of these differences is the same as that found by von Auwers and Ottens (*Ber.*, 1924, **57**, 459) for similar isomerides.

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