

# DIPOLE MOMENTS AS A TOOL IN THE DETERMINATION OF STRUCTURE

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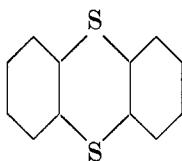
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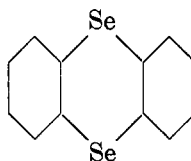
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## I. INTRODUCTION

The determination of dipole moments has contributed very much to the final settlement of problems which arose in classical organic chemistry and to a more intimate knowledge of organic compounds. This has been possible because of the relatively simple correlation between the molecular electric moment and the electric moments of the single links within the molecule, which permits a sufficiently safe evaluation of the experimental figures. The method of dipole moments has even led to conclusions more or less unexpected from the classical point of view; e.g., it has proved that substances like thianthrene (13, 29, 34a, 49, 155, 176) or selenanthrene



Thianthrene



Selenanthrene

(49, 176) are not planar, but have a folded structure; in certain cases this surprising asymmetry has led to the isolation of enantiomorphous forms of quite unknown character (14, 50, 102a, 117, 177). In the following pages, some of the problems which have been or might be solved by means of dielectric measurements are reviewed. Following the lines on which the work in the Daniel Sieff Research Institute is proceeding, the discussion

deals mainly with the use of dipole moments for the solving of stereochemical questions, but, in addition, the detection of zwitter-ion structure in organic molecules by means of the new and simple physical tool of electric moment determinations is considered.

## II. DETERMINATION OF STRUCTURE BY MEANS OF DIPOLE MOMENTS

It is known and need not be reëmphasized here that the *o*-, *m*-, and *p*-disubstituted benzene derivatives are characteristically differentiated by their dipole moments. Hassel and Naeshagen (97) have shown that this also applies to more highly substituted benzene compounds. This is true more especially for those substituents for which the valency linking the substituent to the nucleus coincides with its axis of symmetry,—atoms and groups like CH<sub>3</sub>, CCl<sub>3</sub>, NO, NO<sub>2</sub>, NC, NCO, NSO, NCS, CN, and N<sub>3</sub>,—while in other cases,—substituents like OR, SR, COOR, CHO, CONH<sub>2</sub>, SCN, SO<sub>3</sub>H, and derivatives,—the situation is much more complicated, owing to the additional degrees of freedom, so that here no absolutely decisive conclusions with regard to the relative position of substituents can be drawn from the dipole moments of the compounds.

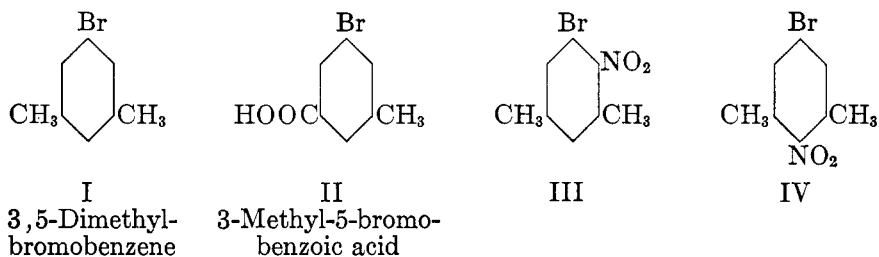
As the structures of practically all the simple di- and poly-substituted benzene derivatives have long been known, the method of dipole moments has not revealed many facts new to the organic chemist.<sup>1</sup> A few examples may show, however, that the method can be easily applied to more complicated cases of this kind and will certainly prove useful in the future.

(1) In an attempt to oxidize 3,5-dimethylbromobenzene (I) (12) with dilute nitric acid, there was obtained, in addition to the expected 3-methyl-5-bromobenzoic acid (II), a neutral product, the analysis of which pointed to the formula C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>NBr of a nitro derivative of I (15)<sup>2</sup>. Of the two possible formulas (III and IV) the dipole moment ( $\mu = 4.00$ ) decided in favor of III<sup>3</sup>. The substance described by Noelting, Braun, and Thesmar (131) as 5-bromo-4-nitro-1,3-dimethylbenzene and melting at 39–40°C. was therefore an impure specimen of the above compound, as its mode of preparation appears to be unambiguous.

<sup>1</sup> Also some important conclusions as to the mutual interactions of ortho substituents.

<sup>2</sup> The substance boiled at 171°C. at 52 mm. and solidified spontaneously. It crystallized from light petroleum in fine needles melting at 53°C. Calculated for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>NBr: C, 41.7 per cent; H, 3.5 per cent; N, 6.1 per cent; Br, 34.8 per cent. Found: C, 41.3 per cent; H, 3.7 per cent; N, 6.4 per cent; Br, 35.2 per cent.

<sup>3</sup> The moment of 2-nitrobromobenzene is 3.98; that of 4-nitrobromobenzene is 2.45 (120).



(2) Guareschi and Biginelli (82) obtained, by the chlorination of 1-bromonaphthalene and by the bromination of 1-chloronaphthalene, a chlorobromonaphthalene, m.p. 119–119.5°C., to which they ascribed—without experimental proof—the structure of the 1,8-compound. As Bergmann and Hirshberg (26) have obtained the real 1-chloro-8-bromonaphthalene (m.p. 94–95°C.) (100) in an unambiguous way (from 1-chloro-8-naphthylamine) and as its dipole moment (2.64) is in accord with this structure, the substance of the Italian authors must have another structure; it may be the otherwise unknown 1,5-compound, which should have a very small dipole moment.

(3) The nitration of  $\beta$ -acetonaphthalide affords, according to Saunders and Hamilton (142), three isomeric nitro-2-naphthylamines. Their structures can be determined not only by purely chemical methods, but also by their conversion into the corresponding nitro-2-halogenonaphthalenes<sup>4</sup> and the determination of their dipole moments. We have proceeded in this way (15). The nitro-2-bromonaphthalene (m.p. 191°C.) corresponding to the nitronaphthylamine melting at 203°C. has a dipole moment of 2.87 and is therefore the 6-nitro compound.<sup>5</sup>

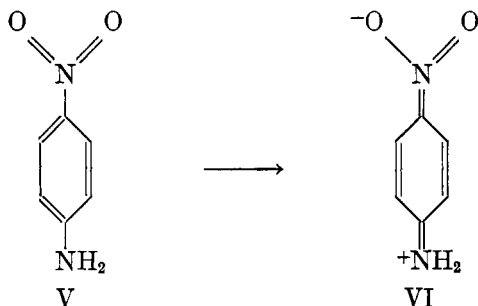
A second and perhaps more interesting problem, which can be solved by dipole moment measurements, is that of the fine structure of certain aromatic substances. (The analogous feature in the urea series has been discussed by Bergmann and Weizmann (34)). It was made clear some time ago (101) that the classical formulas for substituted benzenes are not fully adequate, since, by interaction between the substituents or between the substituent and the nucleus, electrons are shifted within the molecules. Although such an electronic shift will rarely develop into an electron transfer and the formation of a zwitter ion, our problem can be formulated thus: How great is the tendency of a given molecule to undergo transition

<sup>4</sup> As will be shown later, the nitronaphthylamines exhibit certain peculiarities which make their use for this purpose somewhat difficult.

<sup>5</sup> The 2-bromo-1-nitronaphthalene and the 2-bromo-8-nitronaphthalene which might have been formed would have moments of approximately 4.1 and 3.29, corresponding to the *o*- and *m*-bromonitrobenzenes.

to the zwitter-ion state? This formulation makes it clear that the determination of dipole moments can give an important clue to the question, since zwitter ions have an unusually high dipole moment ( $4.774 \times$  the distance of the charges). If too high a dipole moment is observed for a given molecule, one will have to consider the possibility of (a) part of the molecules being in a zwitter-ion state and part behaving "normally," or of (b) all molecules having undergone an electron shift towards the zwitter-ion formula, representing therefore an intermediate resonance state between this and the classical formula. Dipole moments by themselves do not permit a decision between the two alternatives, but other physical evidence (see, e.g., page 560) makes it probable that the second alternative is correct. In the following pages a brief review is given of the pertinent cases known so far.

(1) The moment of *p*-nitroaniline ( $\mu = 6.18$  to  $7.1$ )<sup>6</sup> is higher than the sum of the moments of the two substituents ( $\mu = 5.4$ ). As this sum is the upper limit for a normal *p*-disubstituted benzene, the structural formula V is unsatisfactory and a shift towards VI becomes likely (171).<sup>7</sup>



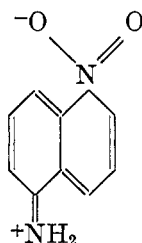
The same is true for *p*-nitrodimethylaniline ( $\mu = 6.87$ ) (126), *p*-nitrodiphenylamine ( $\mu = 5.82$ ) (102), and 4-nitro-4'-aminodiphenyl ( $\mu = 6.46$ ). An important argument that this effect is due to a resonance phenomenon has been put forward by Birtles and Hampson (36; *cf.* 155a, 201). Resonance between two forms can occur only when the atoms concerned remain in practically the same position in both states (152). In a molecule such as nitroaminodurene the plane of the nitro group is, for steric reasons, perpendicular to the benzene ring, while in the form corresponding to formula VI it must be coplanar. As this prevents resonance, nitro-

<sup>6</sup> The moments quoted are taken from the list of dipole moments given in *Transactions of the Faraday Society* **30**, (1934). 4-Aminodiphenyl has a slightly higher moment (1.71; unpublished results, see table 12) than aniline. This may be due to an effect analogous to that in the case of *p*-nitroaniline, owing to the peculiarities of the diphenyl structure, discussed on page 576).

<sup>7</sup> In view of the many factors involved, it is not clear whether the same effect occurs in *o*-nitroaniline ( $\mu = 4.45$  (98);  $\mu = 4.25$  (178)) and in *o*-nitrodiphenylamine ( $\mu = 4.13$ ).

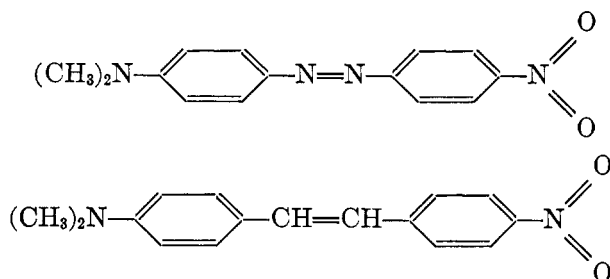
aminodurene should not show the extreme dipole moment of 4-nitroaniline, and this is actually the case ( $\mu = 4.98$ ).

Whether similar effects occur in the naphthalene series is not clear. According to Vasilieff and Syrkin (186),<sup>8</sup> 1-nitro-5-naphthylamine has a moment of 5.22, which is practically equal to the sum of the moments of the substituents. It may be noted that 1-nitro-5-naphthylamine could assume the quinoid formula

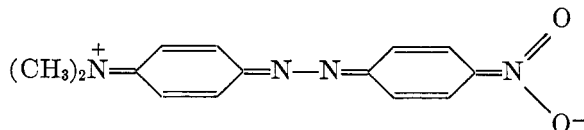


corresponding to II; this structure would represent the system of the unknown 1,5-naphthoquinone, of which derivatives have been prepared (35, 201).

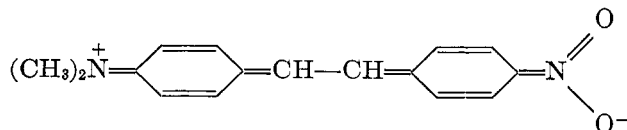
It is clear that other instances may still be found. Thus, A. Weizmann (195) has observed that 4-nitro-4'-dimethylaminoazobenzene and 4-nitro-4'-dimethylaminostilbene



have moments as high as 8.1 and 8.3, owing to forms such as



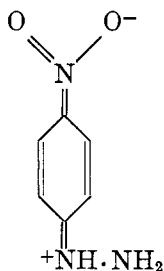
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<sup>8</sup> The remarks made above apply to the moments (4.89; 4.47) reported by them for 2-nitro-1-naphthylamine and 1-nitro-2-naphthylamine, respectively.

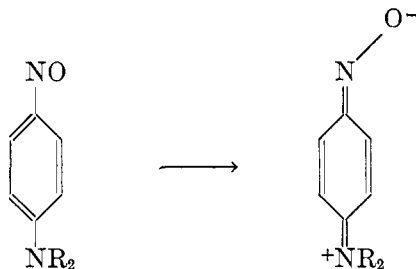
contributing to the resonance state of the molecules. The same conclusion has been drawn recently from the spectra of such stilbene derivatives and from their inability to form stable geometrical isomers (48).

(2) 4-Nitrophenylhydrazine has, according to Ulich and coworkers (183), a dipole moment of 7.2. This is due to a shift towards the structure



which will also occur in the 2,4-dinitro- and 2,4,6-trinitro-phenylhydrazines ( $\mu = 5.8$  and  $4.40$ , respectively).

(3) One of the first anomalies observed (112) was that of the *p*-amino-nitrosobenzenes:

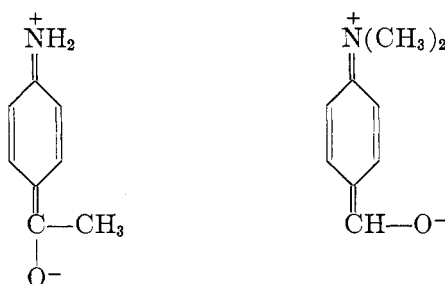


4-Nitroso- <i>N</i> -methylaniline.....	$\mu$ 7.38
4-Nitroso- <i>N</i> -dimethylaniline.....	6.90 (in benzene)
4-Nitroso- <i>N</i> -diethylaniline.....	7.18 (in benzene)

The formula to be postulated is not only formally parallel to the accepted quinone monoxime structure of *p*-nitrosophenol, but it is also in agreement with the chemical behavior of the above substances (easy hydrolysis to quinone monoxime; addition of methyl iodide and of benzoyl chloride at the ends of the charged system), as has been pointed out by E. Bergmann and A. Weizmann (30, 32).

(4) The splitting of the double bond in the carbonyl (and the carboxyl) group is a feature which has been assumed previously. Hence no difficulty arises in ascribing the dipole moment (4.29) (97) of 4-aminoaceto-

phenone and that (5.6) of 4-dimethylaminobenzaldehyde to a shift towards the following structures (194)



and in explaining on similar lines the dielectric behavior of ethyl and methyl 4-aminobenzoates (moments of 4.0 and 3.3) (71) and of 4-amino-

TABLE 1

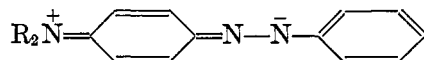
SUBSTANCE	FORMULA	$\mu$
4-Dimethylaminocinnamaldehyde.....	$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHCHO}$	5.4
4-Dimethylaminobenzylideneacetone...	$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHCOCH}_3$	5.3
4-Dimethylaminocinnamylideneacetone, m.p. 120°C.....	$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHCH}=\text{CHCOCH}_3$	6.7
4-Dimethylaminobenzylideneacetophenone.....	$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHCOC}_6\text{H}_5$	4.4
4-Dimethylaminocinnamylideneacetophenone.....	$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHCH}=\text{CHCO-C}_6\text{H}_5$	5.4
Ethyl 4-dimethylaminocinnamate.....	$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHCOOC}_2\text{H}_5$	4.7

benzamide ( $\mu = 4.7$ ) (61). The Raman spectra of the benzoic acid esters lead to similar conclusions (131). A. Weizmann (194) has shown recently that the same effect is still more marked when the distance between the amino and the carbonyl groups is increased by the interposition of vinylenic groups. This may be concluded from table 1.

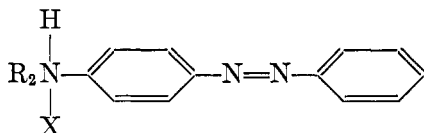
It has also been suggested that the intense colors which the unsaturated carbonyl compounds listed in table 1 develop on contact with concentrated sulfuric acid are due to fixation of the elements of the acids to the ends of the charged chain, as is the case with the aminoazo dyes (see below).

(5) *Aminoazo dyes*. E. Bergmann and A. Weizmann (30, 32) have observed that aminoazo dyes such as 4-aminoazobenzene ( $\mu = 2.71$ ), 4-dimethylaminoazobenzene ( $\mu = 3.68$ ), 4-benzeneazo-1-naphthylamine ( $\mu = 2.50$ ), and 1-benzeneazo-2-naphthylamine ( $\mu = 2.14$ ) have dipole

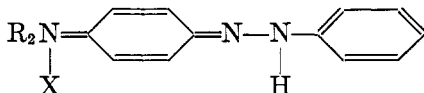
moments much higher than expected; as azobenzene (see page 578) has no finite dipole moment, the dipole moments of these azo dyes, in their classical formulas, should be those of aniline ( $\mu = 1.55$ ) and of the  $\alpha$ - and  $\beta$ -naphthylamines ( $\mu = 1.44$ ;  $\mu = 1.74$ ), respectively. All must therefore be formulated as follows:<sup>9</sup>



This formula agrees with the behavior of the aminoazo dyes towards acids. Hantzsch (88, 89, 90, 103) has discovered that they form two series of salts, yellow and violet ones, which have been formulated by the author as



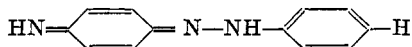
and



and which would be formed by the addition of HX to the normal and to the zwitter-ion formula, respectively. Furthermore, it is important that dimethylaminoazobenzene has a spectrum which is different from that of azobenzene, while that of its yellow hydrochloride coincides completely with the spectrum of azobenzene (90). This shows at the same time that we must assume that all of the molecules have undergone the electron shift towards the zwitter-ion formula; otherwise, one would expect that the spectrum of the aminoazo dye would be composed of the azobenzene spectrum and a superimposed second one corresponding to the zwitter-ion molecules.

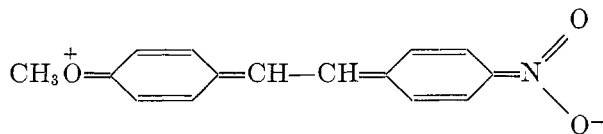
(6) *Methoxy compounds.* It is clear that the effects discussed above will not be restricted to amino compounds, but will apply to those substituents in which unshared electrons are present, e.g., in hydroxy and alkoxy compounds. For 4-nitro-4'-methoxystilbene and 4-nitro-4'-methoxyazobenzene, this has been postulated on the basis of spectroscopic evidence (75), and recent experiments by A. Weizmann (195) confirm this assumption; only an electron shift towards the structures

<sup>9</sup> In the case of the non-methylated azo dyes a transfer of hydrogen would be possible, leading to a quinone imine phenylhydrazone structure,

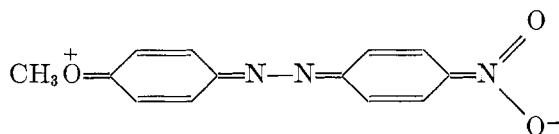


but this would place the amino and the dialkylamino compounds in two different classes, which is certainly not justified.

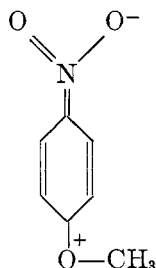




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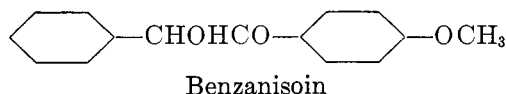
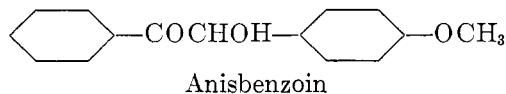


would explain the dipole moments (7.8 and 6.5) observed. Even in simpler molecules dielectric indications to the same effect are already known, although they are not very marked. 4-Methoxyazobenzene, for example, has a moment slightly greater than that of anisole ( $\mu = 1.29$  (30, 32, 189) as compared with 1.16 and 1.23 (64, 98, 189)). Similarly, the anomaly that the dipole moment falls from *o*-nitroanisole to *m*-nitroanisole, but rises again to *p*-nitroanisole (57) will be rightly ascribed to a shift in the latter substance towards



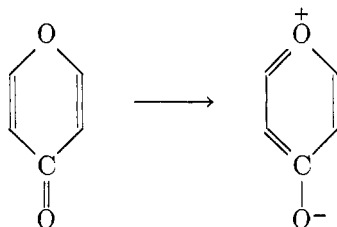
For *o*-hydroxyazo dyes, a zwitter-ion formula has been temporarily postulated by R. Kuhn (108), but their dipole moments show no indication to that effect (30, 32). *p*-Hydroxyazobenzene has in benzene solution a moment (1.62) identical with that (1.61) of phenol (63), but in dioxane solution a markedly higher one (2.04). Whether this is due to a shift towards the zwitter-ion formula or to a tautomeric change to a quinone hydrazone structure remains undecided.

An interesting illustration of the problem discussed is provided by the difference in the stability of anisbenzoin and of benzanisoin:

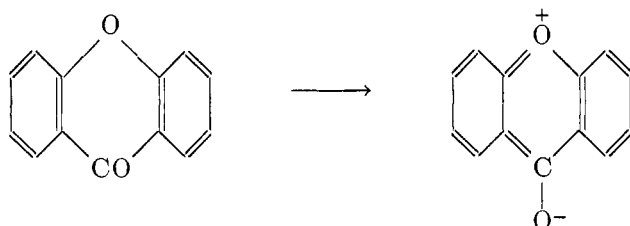


The latter is more stable because of the interaction between the methoxyl and carbonyl groups through the benzene ring, which is made impossible in anisbenzoin by the interposition of the CHOH group (11).

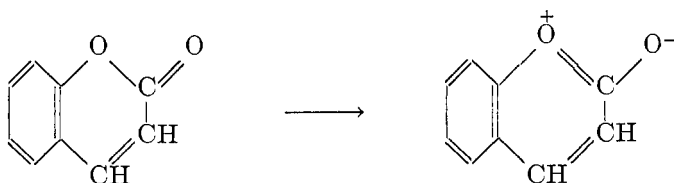
(7) In a less definite form, the conclusion that the classical formula must be replaced by a zwitter-ion structure has been drawn previously in the  $\gamma$ -pyrone series in order to explain certain chemical peculiarities (30, 32): the reaction of  $\gamma$ -pyrone with methyl iodide and with methylmagnesium iodide, both of which add to the ends of a charged system,



and the inactivity of pyrones and xanthenes

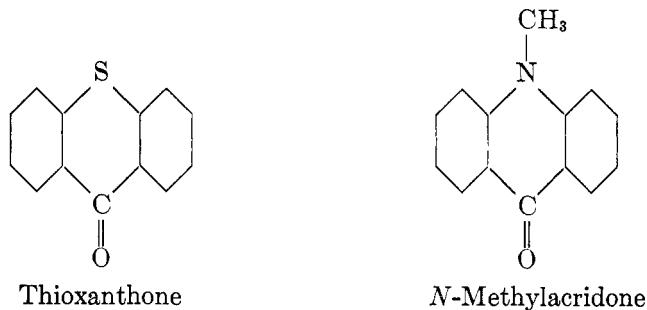


towards certain carbonyl reagents. The dipole moments of 2,6-dimethylpyrone ( $\mu = 4.05$  (99), 4.48 (137), 4.6 (111), 4.62 (185)), 2,6-diphenylpyrone ( $\mu = 3.82$  (99, 111)), and xanthone ( $\mu = 3.07$  (30, 32), 3.0 (111), 2.9 (137, 185), 3.11 (110)) are higher than the difference between those of the carbonyl group and of the ether oxygen ( $3.05 - 1.13 = 1.92$ ), which again points to a zwitter-ion formula. The same is true for 2,6-diphenylthiopyrone, of which the moment is 4.39 (4), while the difference between the dipole moments of the carbonyl and the sulfide is ( $3.05 - 1.51 =$ ) 1.54. In the same way, the excess in the moment of coumarin and of 3-phenylcoumarin (111, 136, 185) over the theoretical value (resultant from the  $\text{C}-\text{O}-\text{C}$  moment and the  $\text{C}=\text{O}$  moment interacting at about  $60^\circ$ ) is to be explained by a shift according to the scheme

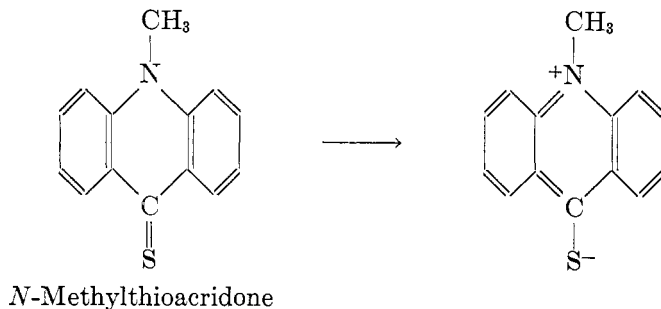


by which—as in the case of xanthone—a more fully aromatic (naphthalenoid) structure is produced. Analogous conclusions have been drawn from the Raman spectra of these substances by Volkenshtein and Syrkin (187).

These observations have recently been extended by A. Weizmann (195) to include thioxanthone and *N*-methylacridone ( $\mu = 5.4$  and  $3.5$ , respectively).



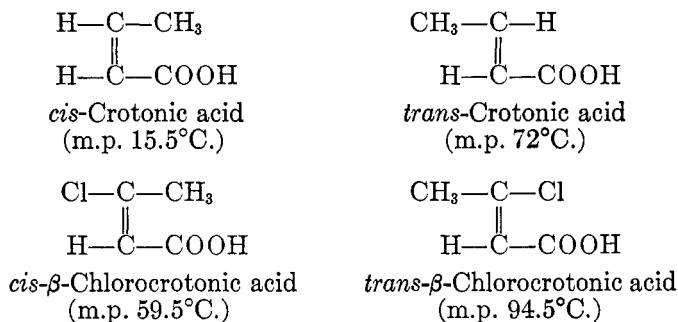
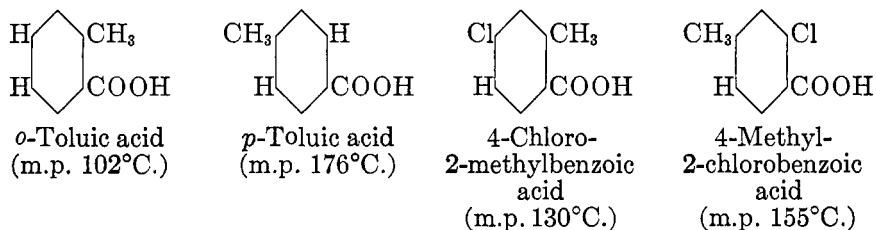
This effect is still more pronounced for the corresponding thioketones,—xanthione, thioxanthione, and *N*-methylthioacridone,—of which the dipole moments are 5.4, 5.2, and 5.2, respectively. These measurements, however, do not indicate what Gleu and Nitzsche (79) have postulated recently on the basis of chemical evidence, namely, that *N*-methylthioacridone exists exclusively in the form of a zwitter ion:



### III. THE ETHYLENIC DOUBLE BOND

The methods used in classical organic chemistry for assigning configurational formulas to ethylenic isomers were mostly based on the comparison of certain physical properties, of which none, however, had a theoretically founded relationship to the geometrical structure. This is especially conspicuous in those cases where not all of the possible geometric isomers are preparatively accessible. One of the methods (A. Werner (197)), however, may be mentioned, as it resembles the application of dipole moment measurements. The *cis*-isomers are compared with the

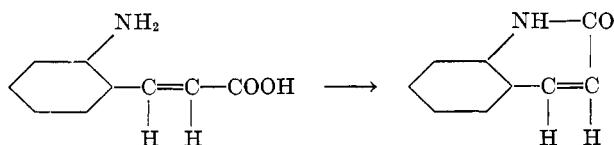
ortho compounds and the *trans*-isomers with the para compounds containing the same substituents: since *o*-toluic acid has a lower melting point than the para compound and 4-chloro-2-methylbenzoic acid a lower one than 4-methyl-2-chlorobenzoic acid, it is concluded that the lower melting forms of crotonic acid and  $\beta$ -chlorocrotonic acid are the *cis*-forms (with regard to the relative positions of the methyl and carboxyl groups).



It is clear that this rule cannot be generally valid, as the melting point is not a function of the geometrical structure of the molecule only. This criterion is, furthermore, inapplicable in cases where only one of the geometrical isomers is known.

The only exact method of configurational analysis known in classical organic chemistry was that based on ring-closure reactions. If, of two isomers, only one is capable of forming a ring between two substituents, it is clear—in view of the rigidity of the double bond—that these two substituents must lie on the same side of the plane of the double bond.<sup>10</sup>

<sup>10</sup> Besides the much-quoted case of the pair maleic acid–fumaric acid, the *o*-amino-cinnamic acids may be recalled, only one of which is able to form a cyclic lactam and therefore is the *cis*-form (162):

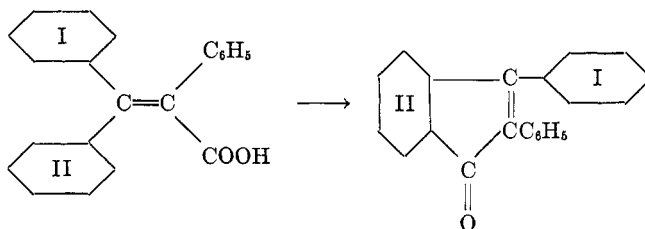


Analogously, Shriner and Sharp (151) have recently ascribed a *trans*-structure to

Even in those cases where both isomers are capable of forming the same cyclic product—one of them obviously by steric rearrangement, owing to the conditions of reaction—the different ease of reaction is indicative of the configuration of the starting materials: the form which is capable of cyclization without previous change in configuration will always cyclize more easily. It is evident that in such a case a conclusion can be drawn only when both isomers can be compared. A good example is furnished by the isomeric  $\alpha,\beta$ -dibromocinnamic acids: one of them cyclizes under the influence of sulfuric acid at room temperature, the other one on distillation with phosphorus pentoxide, both to give the same 2,3-dibromoindone (78, 109, 139).<sup>11</sup>

the *o*-hydroxybenzalacetone which is formed from the non-lactonizable *trans*-*o*-hydroxycinnamic acid and methylmagnesium iodide.

Another interesting example has been studied by Koelsch (105). The  $\alpha,\beta$ -diphenylcinnamic acids are capable of forming 2,3-diphenylindones:



When rings I and II are different (differently substituted), the two isomers give different diarylindones, the structures of which give a lead to the assignment of configurational formulas to the isomeric acids: the ring forming the indone skeleton must have been near the carboxyl group, which appears as carbonyl in the resulting molecule. The following pairs have been studied:  $\alpha,\beta$ -diphenyl- $\beta$ -(*p*-methoxyphenyl)acrylic acids,  $\alpha,\beta$ -diphenyl- $\beta$ -(*p*-chlorophenyl)acrylic acids, and *cis*- $\alpha,\beta$ -diphenyl- $\beta$ -(*p*-tolyl)acrylic acid.

<sup>11</sup> For the corresponding  $\alpha,\beta$ -dichlorocinnamic acids, of which the isomer melting at 121°C. is cyclized easily, see Roser and Haselhoff (139). In other cases only one of the isomeric forms is cyclized, while the other one remains unchanged or is decomposed under the same conditions:  $\alpha$ -chlorocinnamic acid (m.p. 110–111°C.) gives  $\alpha$ -chlorotruzone (dimer of 2-chloroindone) (125);  $\alpha$ -bromocinnamic acid, m.p. 120°C., behaves analogously (118, 124);  $\alpha$ -methylcinnamic acid (m.p. 91–92°C.) (167);  $\beta$ -methylcinnamic acid (m.p. 131.5°C.) (165);  $\alpha,\beta$ -dimethylcinnamic acid (39, 46).

For the sake of completeness, it may be noted that substitution reactions on ethylenic compounds can hardly be used for the determination of configuration, as it is not known whether they proceed with or without change of configuration. Thus, the conversion of the diiodoethylenes by means of potassium cyanide into maleic acid dinitrile and fumaric acid dinitrile, respectively, does not itself prove that the diiodo compounds have the same structure, although in this case it is true (104). The comparison of velocities of substitution is even less worthy of confidence, although it has often been used, as may be seen from the following examples: *cis*-



The *trans*-compounds are characterized by a dipole moment of 0 or by a small moment, the *cis*-forms by a finite electric moment. For 1-chloro-2-iodoethylene Errera (70) has assumed that the higher moment corresponds to the *trans*-form, supposing that the iodine atom is "positively charged with regard to the chlorine atom," i.e., that the direction of the C—Cl moment is not the same as that of the C—I moment, but this conclusion seems to be unfounded, as may also be seen from the comparison of the moments of, for instance, *o*- and *p*-bromiodobenzenes (188): the ortho compound, which corresponds very closely to the *cis*-form, has a higher moment (1.73; 1.86) than the para isomer ( $\mu = 0.49$ ) (22, 72, 190).

TABLE 2A

SUBSTANCE	FORMULA	MELTING POINT	$\mu$	REFERENCE
<i>p</i> -Chlorodiphenylvinyl bromide...	$\begin{array}{c} \text{ClC}_6\text{H}_4 \\ \diagdown \\ \text{C}=\text{CHBr} \\ \diagup \\ \text{C}_6\text{H}_5 \end{array}$	°C. 94-95	2.27	(21)
		43-44	1.28	(21)
<i>p</i> -Bromodiphenylvinyl bromide...	$\begin{array}{c} \text{BrC}_6\text{H}_4 \\ \diagdown \\ \text{C}=\text{CHBr} \\ \diagup \\ \text{C}_6\text{H}_5 \end{array}$	109	2.43	(21)
		42-44	1.22	(21)
<i>p</i> -Chlorotriphenylvinyl bromide...	$\begin{array}{c} \text{ClC}_6\text{H}_4 \\ \diagdown \\ \text{C}=\text{CBrC}_6\text{H}_5 \\ \diagup \\ \text{C}_6\text{H}_5 \end{array}$	160	2.61	(17)
		119	1.57	(17)

A discussion of the absolute magnitude of the dipole moments of the *cis*-forms lies outside the scope of this review; it depends on the state of resonance between the classical and some other structural formulas (65, 153).

In table 2A a second group of dihalogenated olefins is listed, which shows a surprising feature. The *cis*-forms have the expected dipole moments, but their isomers have, instead of zero moment, a moment approximately half of that of the *cis*-configuration. E. Bergmann (17) has suggested that the compounds characterized by the lower moments are molecular compounds of the *cis*- and the (unknown) *trans*-forms and therefore show half of the dipole moment of the former. These combinations, therefore, resemble in a certain way the racemic compounds built up from a levo- and a dextro-rotatory form.

We feel sure that this new stereochemical effect is not restricted to the three pairs listed in table 2A, but that in many cases, e.g., in the series of the substituted cinnamic acids, similar conditions prevail. In the above-quoted paper of Koelsch (105), some indications to that effect may be found. Koelsch has observed that his substituted triphenylvinyl bromides, although appearing homogeneous, on successive reaction with magnesium and carbon dioxide give mixtures of the two isomeric corresponding diarylcinnamic acids. Theoretically, it is possible that such substitution reactions are accompanied by partial inversion of configuration, but it may well be that the apparently homogeneous triphenylvinyl bromides actually were molecular compounds of the possible geometrically isomeric forms.

In their extensive photochemical studies, Stoermer and coworkers (159, 160, 161) have observed some interesting cases in which the geometrical isomers of substituted cinnamic acids, on irradiation, produce "mixed forms":  $\beta$ -methylcinnamic acid (melting point of the mixed form, 76°C.);  $\beta$ -ethylcinnamic acid (m.p. 62–63°C.); *o*-methoxy- $\beta$ -methylcinnamic acid (m.p. 76–78°C.);  $\beta$ -*p*-dimethylcinnamic acid (m.p. 94–96°C.) (compare Lindenbaum (119));  $\beta$ -propylcinnamic acid (m.p. 59–60°C.). In the case of  $\alpha,\beta$ -dimethylcinnamic acid the synthesis (141) yielded a solid and a liquid form. O. Blum-Bergmann (39), however, showed that, under suitable conditions, the two isomers (melting points 108.5–110°C. and 105–107°C.) can be obtained separately in crystalline form.

The tendency to form such molecular compounds seems somewhat characteristic for the whole group. We have observed that *trans*- $\alpha,\beta$ -dibromostilbene (m.p. 206–208°C.) gives with toluene a molecular compound (ratio 1:1; m.p. 195°C.), according to figure 1, and that in the bromination of toluene a molecular compound (ratio 1:2; m.p. 77°C.) is formed with *cis*- $\alpha,\beta$ -dibromostilbene (m.p. 68°C.) (150).<sup>12</sup> *cis*- $\alpha,\beta$ -Dichlorostilbene (m.p. 60°C.) and toluene give an analogous molecular compound (ratio 2:1; m.p. 67–69°C.).<sup>13,14</sup>

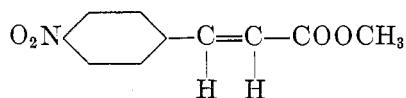
<sup>12</sup> The substance was recrystallized from methyl alcohol as long needles and was identified by analysis. (Calculated for  $C_{12}H_{10}Br_2$ : C, 59.0 per cent; H, 3.5 per cent. Found: C, 59.3 per cent; H, 3.7 per cent.)

<sup>13</sup> This substance was also recrystallized from methyl alcohol. Calculated for  $C_{12}H_{10}Cl_2$ : Cl, 21.0 per cent. Found: Cl, 20.9 per cent.

<sup>14</sup> It may perhaps be surprising that in the above cases the "cis"-compounds have the higher melting point, but it must be recalled that the *cis*-structure refers to the two highly polar substituents in the molecule only, while the melting point may be influenced by the other substituents too. Furthermore, the melting point regularities need not be valid throughout, and it is interesting that Stoermer and Simon (166) have already observed that ultraviolet light converts the high-melting *p*-bromodiphenylvinyl bromide into the lower melting form. As they assigned, on the basis of the temperature of melting only, the *trans*-structure to the high-melting form, they saw in this conversion an irregularity, but actually here, as in other cases, ultraviolet light produces the reaction *cis*  $\rightarrow$  *trans*.





Methyl 4-nitro- $\alpha$ -phenylcinnamate

That the dipole moment of the above compound is slightly higher than that of ethyl 4-nitrocinnamate corresponds to the fact (17) that ethyl cinnamate also has a slightly lower moment than methyl  $\alpha$ -phenylcinnamate.<sup>16</sup>

The two  $\beta$ -bromocinnamic acids are formed by the addition of hydrobromic acid to phenylpropionic acid. In contradistinction to the findings of Sudborough and Thompson (170), we have observed that *cis*-addition is slightly favored. Stereochemically, it is interesting that debromination

TABLE 3\*

SUBSTANCE	MELTING POINT	$\mu$	REFERENCE
	°C.		
Methyl $\alpha, \beta$ -dibromocinnamate . . . . .	100	2.68	(17)
	134	1.89	(17)
Methyl $\beta$ -bromocinnamate . . . . .	159	2.63	(17)
	130	1.81	(17)
(4-Bromobenzal)acetophenone . . . . .	120	2.47	(17)
(4-Bromobenzal)-4'-bromoacetophenone . . . . .	185-186	2.03	(17)
$\alpha, \beta$ -Dibromobenzalacetophenone . . . . .	113-114	3.17	(17)
$\beta$ -Bromobenzalacetophenone . . . . .	B.p. 220° at 14 mm.	3.59	(17)
Ethyl 4-nitrocinnamate . . . . .	140	3.50	(17)
Methyl 4-nitro- $\alpha$ -phenylcinnamate . . . . .	224.5	3.78	(17)
Dimethyl maleate . . . . .	130	2.55; 2.51	(154); (41)
Dimethyl fumarate . . . . .	286-287	2.39; 2.23	(154); (41)
Dimethyl citraconate . . . . .	91	2.68	(42)
Dimethyl mesaconate . . . . .	202	2.06	(42)
4,4'-Dimethoxyisostilbene† . . . . .	38	1.77	(150)

\* As far as esters are concerned, the melting points refer to the corresponding acids.

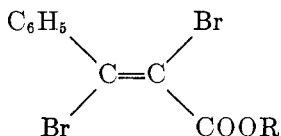
† The isomeric form, m.p. 213°C., was too insoluble to be measured.

of the *cis*-acid (m.p. 159°C.) (which contains phenyl and carboxyl in the *trans*-position with respect to each other) gives mainly *cis*-cinnamic acid, while debromination of the *trans*-acid (m.p. 130°C.) gives *trans*-cinnamic acid; debromination is therefore accompanied by configurational inversion. This may be due to a peculiarity in the substitution of bromine by hydrogen or—more likely—to the fact that no substitution occurs at all, but rather addition of hydrogen to the double bond and subsequent removal of hydrogen bromide (see note 11).

<sup>16</sup> The *trans*-structure of this compound follows from the fact that *o*-amino- $\alpha$ -phenylcinnamic acid, which on deamination gives the isomeric  $\alpha$ -phenylcinnamic acid, easily forms a lactam and is therefore the *cis*-compound (158).

Another interesting point may be raised in this connection: The two oximes of the *p*-bromocinnamaldehyde which is obtained (exclusively) upon the addition of hydrobromic acid to phenylpropionaldehyde give with acetic anhydride the nitrile of the  $\beta$ -bromocinnamic acid, m.p. 159°C. (*trans*-acid), and with phosphorus pentachloride the nitrile of the isomeric acid (m.p. 130°C.) (9). It will be interesting to determine the moment of the halogenated aldehyde and so to obtain an insight into the steric mechanism of these dehydration reactions.

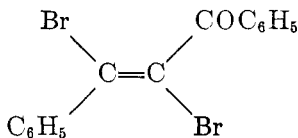
The configuration of the two  $\alpha, \beta$ -dibromocinnamic acids follows from the consideration that the ester



in which the moments of the two bromine atoms cancel each other must have the smaller moment and about the same as that of ethyl cinnamate. This is the ester of the acid melting at 154°C. The isomeric ester, as would be expected, has a higher moment. In this case the same configurations have been assumed previously for other reasons (easier cyclization of the acid melting at 100°C.; other, less conclusive, arguments have been advanced by Stoermer and coworkers (163, 164)). Here, too, the old rule (3, 198) that *trans*-compounds have a weaker absorption than the *cis*-forms is true to the extent that the *cis*-acid is actually yellow.<sup>17</sup>

In the formation of the  $\alpha, \beta$ -dibromocinnamic acids from phenylpropionic acid and bromine, *trans*-addition prevails, which is contradictory to a widespread assumption (122).<sup>18</sup>

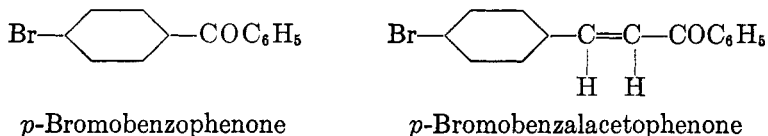
Analogous reasoning permits an evaluation of the dipole moments of the benzalacetophenone derivatives listed in table 3. The dipole moment of  $\alpha, \beta$ -dibromobenzalacetophenone is near enough to that of benzalacetophenone ( $\mu = 2.93$ ) (17) to justify the conclusion that the two bromine moments cancel each other and therefore that the bromine atoms must be in the *trans*-position to each other; here again, in the addition of



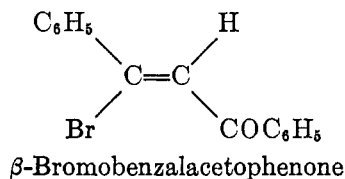
<sup>17</sup> This is by no means generally so. For example, on the basis of this rule Arends (3) has assigned incorrect structures to the  $\alpha, \beta$ -dichloro- and  $\alpha, \beta$ -dibromo-stilbenes.

<sup>18</sup> Ayyar (1) has recently claimed that the free phenylpropionic acid adds bromine in the *cis*-position, while its esters add bromine in the *trans*-position. The first part of this statement is not in accord with our findings.

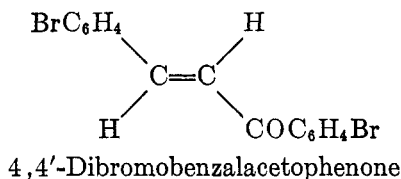
bromine to phenylbenzoylacetylene, the *trans*-reaction is favored.  $\beta$ -Bromobenzalacetophenone and *p*-bromobenzalacetophenone have too different moments for an analogous configuration. As the moment of the latter is close to that of *p*-bromobenzophenone ( $\mu = 2.75$ ) (21), it contains the two polar groups in the *trans*-configuration.



$\beta$ -Bromobenzalacetophenone, b.p. 219-220°C. at 14 mm, is therefore a *cis*-form,

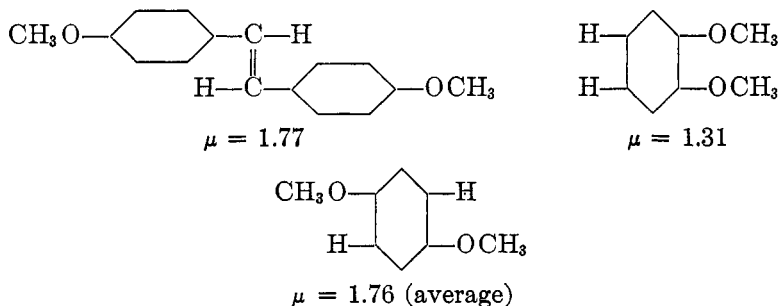


4,4'-Dibromobenzalacetophenone, m.p. 185-186°C., is the *trans*-compound,



as its dipole moment (2.03) is not very different from that of 4,4'-dibromobenzophenone ( $\mu = 1.69$ ) (21).

The dipole moment of the low-melting 4,4'-dimethoxystilbene, on the basis of the same reasoning, would unexpectedly point to the *trans*-configuration, as it is much nearer to that of *p*- than to that of *o*-dimethoxybenzene (93, 95, 191), but this conclusion should await confirmation by determination of the moment of the higher melting isomer, which unfortunately is very slightly soluble in non-polar solvents.



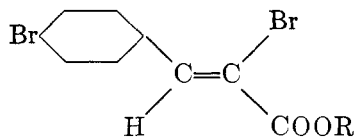
From the inspection of the pairs maleate-fumarate and citraconate-mesaconate it follows that here too, where the theoretical dipole moments are not easily calculated, owing to the interactional forces between the polar groups, the *trans*-compound has the lower dipole moment. This agrees with the fact that diethyl *o*-phthalate has a higher moment (2.6) than diethyl terephthalate (2.2) (72, 193) and will be used later for configurational assignment in a more complicated dicarboxylic acid (see page 578).

In a number of cases, presented in table 4, no conclusions as to configuration can be drawn from the measured dipole moments, as the polar substituents are linked to the same olefinic carbon atom.

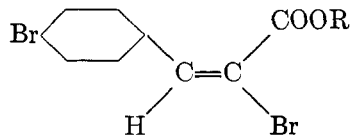
TABLE 4

COMPOUND	PHYSICAL CONSTANTS	$\mu$
4-Bromostilbene . . . . .	M.p. 31°C.; liquid	1.38
$\alpha$ -Bromobenzalacetophenone . . . . .	B.p. 218-219°C. at 14 mm.	1.38
Ethyl $\alpha$ -bromocinnamate . . . . .	M.p. (acid) 130-131°C.	2.25
	M.p. (acid) 120°C.	2.80

A decision would be possible if the analogs bearing a polar substituent on the neighboring olefinic carbon atom were prepared according to exactly the same preparative procedure. In this case, assignment of configurational formulas would be possible, and by analogy the structure of the above substances would be made clear.  $\alpha$ -Bromocinnamic acid, melting at 130-131°C., is prepared from phenylpropionic acid and gaseous hydrogen bromide in benzene solution. It should be analogous to the isomeric form of 4, $\alpha$ -dibromocinnamic acid, which is obtained from 4-bromopropionic acid and hydrogen bromide under the same conditions:



(expected moment = 2.7)<sup>19</sup>



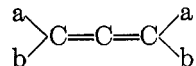
(expected moment = 1.9)<sup>19</sup>

In the same way, the form which would be obtained from 4-bromocinnamic acid dibromide and potassium hydroxide solution would be analogous to the  $\alpha$ -bromocinnamic acid, m.p. 120°C., which is formed analogously from cinnamic acid dibromide. In a parallel manner, the interesting  $\alpha$ -halogenocinnamaldehydes (7) could be studied from the stereochemical viewpoint.

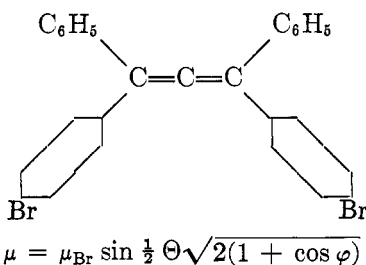
<sup>19</sup> Corresponding to those of the methyl  $\alpha,\beta$ -dibromocinnamates.

*The allene system*

According to van't Hoff, an allene of the type



should be resolvable into optical antipodes; the two pairs of substituents should lie in two planes perpendicular to each other. The numerous failures to realize optical activity of this kind have eventually led to the suggestion (73) that van't Hoff's prediction is incorrect and that the allene molecule is planar. This general question could be answered by measurements of dipole moments: if in the above formula the two substituents b, e.g., are polar, while a makes no finite contribution to the electric moment of the molecule, the spatial angle,  $\varphi$ , between the C—b valencies and, accordingly, the molecular electric moment, would be different in the diplanar and the planar models. E. Bergmann and Hampson (24) have carried out this investigation, taking into account that the planar model formally would give rise to two configurations, corresponding to a *cis*- and a *trans*-form (angles between the C—b vectors  $0^\circ$  and  $180^\circ$ , respectively). After having shown that the tetraphenylallene system in itself has no dipole moment, the authors derived the following equation for the dipole moment of 1,3-di(*p*-bromophenyl)-1,3-diphenylallene



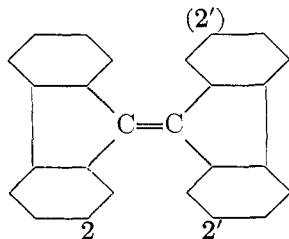
where  $\Theta$  is the "apparent" angle between the two substituents at the same carbon atom. This has been derived from the dipole moment (1.57) of 1,1-di-*p*-chlorophenyl-3,3-diphenylallene, which is due to two chlorine moments inclined at the angle  $\Theta$ . The value of approximately  $120^\circ$ , thus found, is in good accord with dipole measurements in the series of benzophenone and 1,1-diphenylethylene (21) and with figures obtained by other physical methods (121, 157, 169).

For the classical model ( $\varphi = 90^\circ$ ) the theoretical value of  $\mu$  is 1.85, and for the two non-classical possibilities is 0 and 2.62, respectively. The dipole moment actually found was 1.96, so that van't Hoff's model is certainly correct. Subsequently, Maitland and Mills (123), Kohler, Wal-

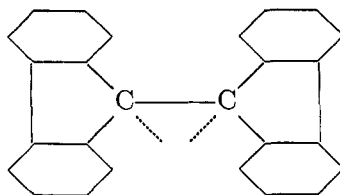
ker, and Tishler (106), and Kohler and Whitcher (107) succeeded in preparing optically active forms of substituted allenes, thus giving final support to the theory of the tetrahedral carbon atom.

*2,2'-Difluorodibiphenyleneethylene*

A similar problem was encountered in the study of the 2,2'-difluoro derivative of the dark red dibiphenyleneethylene.

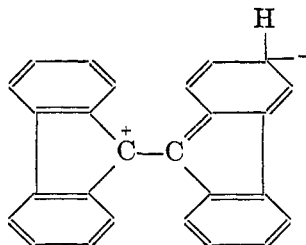


From the orthodox point of view, this substance should exist in two *cis-trans* isomeric forms, but none of the compounds of the fulvenic type has been obtained in geometrically isomeric forms (see, recently, Gleu and Nitzsche (80)), a failure which points to the possibility suggested by Bergmann and Engel (20) that these forms are easily interconvertible through an intermediate step in which the rigidity of the double bond is temporarily cancelled, e.g., through a diradical form (compare Burawoy (45)).

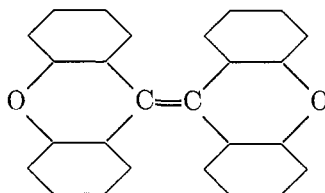


As it seemed interesting to determine the actual configuration of the one isolable form of the above ethylene, its dipole moment was determined. While its *trans*-form should obviously have a zero moment, and its *cis*-form a moment of 2.90, a moment of 2.51 was actually observed (16). The molecule, therefore, would have neither the *cis*- nor the *trans*-configuration, but an intermediate twisted configuration, incompatible with an ethylenic formula at all. One could assume that the molecules (or at least part of them) have constantly a diradical form, but Farkas and Sandler (74; *cf.* 146) were unable to detect paramagnetic properties. It may therefore be that another formula applies, e.g., that of a zwitter ion.<sup>20</sup>

<sup>20</sup> In a discussion in Manchester (November, 1938) Dr. Evans pointed out that these two formulas are not different, but that both represent extreme forms of the same resonance state.

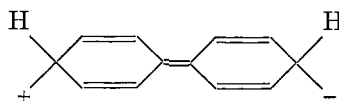


A similar suggestion has been put forward by Schoenberg and coworkers (148, 149) in order to explain the observation that the practically colorless dixanthylene



is converted by heat into a dark blue form. (For "thermochromic ethylenes" in general, see Bergmann and Corte (19)). It will be interesting to study the dipole moments of appropriate representatives of this and similar series (see also page 557).

This position would not be unique, since in the case of diphenyl (and similar substances) analogous conditions prevail. One must assume that other structures besides the classical contribute to the structure of diphenyl, such as



as has been suggested frequently, in order to explain the propagation of effects from one nucleus into the other and to explain the absorption spectra of derivatives of diphenyl (47, 77, 116, 135, 172, 181). A detailed investigation of the spectra of such "fulvenes" as the above would therefore also be of interest.

#### IV. STEREOISOMERISM IN RING SYSTEMS

As in the case of ethylenes, non-aromatic ring systems bearing two or more substituents give rise to isomerism, and if the substituents are of polar character, the determination of the molecular electric moment enables us to determine the steric arrangement of the substituents. A characteristic case has recently been reported by E. Bergmann and A. Weiz-



mann (33). The addition of chlorine to 1,5-dichloro-, to 9,10-diphenyl-, and to 1,8-dichloro-anthracenes produces dichlorides having dipole moments of 3.7, 3.0, and 2.4, respectively. This means that in the first two cases the halogen adds in the *cis*-position, and in the latter in the *trans*-position (as the moment of 1,8-dichloroanthracene by itself is 3.2, 1,5-dichloro- and 9,10-diphenyl-anthracenes obviously having zero moments). The surprising *cis*-addition is ascribed by the above authors to the possibility that the chlorine molecule as such is able to enter the space between the 9,10-positions, just as oxygen, maleic anhydride, and similar substances do,<sup>21</sup> while usually halogens add to unsaturated systems by an atomic or ionic mechanism. (For a general review, see 2, 18, 129, 179, 180.)

TABLE 5

SUBSTANCE	MELTING POINT	$\mu$	CONFIGURATION	REFERENCE
	°C.			
1,4-Dichlorocyclohexane.....	102	0	<i>Trans</i>	(84)
1,4-Dibromocyclohexane.....	111	0	<i>Trans</i>	(84, 94)
1,4-Diiodocyclohexane.....	67.5	2.4	<i>Cis</i>	(84, 94)
	142	0	<i>Trans</i>	(84, 94)
Dihydrocyclopentadiene-1,2-dibromide....	66	3.20	<i>Cis</i>	(62)
Dihydro- $\alpha$ -tricyclopentadiene-1,2-dibromide..	107	3.28	<i>Cis</i>	(62)
Dihydro- $\beta$ -tricyclopentadiene-1,2-dibromide..	123	3.26	<i>Cis</i>	(62)
Dihydro- $\beta$ -tricyclopentadiene-1,2-dibromide..	106	2.06	<i>Trans</i>	(62)
1,2,4,5-Tetrabromocyclohexane.....	185	2.22		(85)

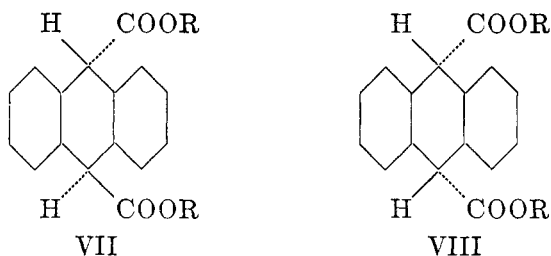
In the preceding section it has been reported that tolane is able to form molecular compounds with the corresponding dihalogen addition products, and for substances interconvertible by the addition or elimination of hydrogen similar effects (formation of mixed crystals) have been known for a long time, provided the substances have a certain geometrical resemblance (44, 66). One of the geometrically isomeric forms of a 1,2-disubstituted ethylene is always more similar to the corresponding acetylene and ethane derivatives. It is therefore interesting that aromatic substances sometimes show an analogous affinity to one of their dihydro derivatives. Haack (83) has observed this for 9-phenyl- and 9,10-diphenyl-anthracenes; even before, it was known that naphthalene and 1,4-dihydronaphthalene give a crystalline molecular compound upon the incomplete reduction of naphthalene (10) or upon the addition of lithium to naphthalene.

Other similar cases of disubstituted isocyclic ring systems are listed in table 5.

<sup>21</sup> In the case of 1,8-dichloroanthracene the chlorine atoms present may interfere with this mechanism.

The conclusions drawn as to configurations are self-evident. For the 1,2,4,5-tetrabromocyclohexane the dipole moment in itself is not decisive, but it is in accord with the results of an x-ray study of the compound.

In an analogous manner, the moments of substances containing "irregular" substituents (page 554) can be evaluated. The difference in dipole moment between the two dimethyl 9,10-dihydroanthracene-9,10-dicarboxylates (33) (namely, 2.6 and 1.7) points to the *cis*-structure (VIII) for the former ( $\beta$ ) (melting point of the acid, 294°C. (with decomposition); melting point of the ester, 163.5–165°C.) and to the *trans*-structure (VII) for the latter ( $\alpha$ ) (melting point of the acid, 286°C. (with decomposition); melting point of the ester, 162.5–163°C.). This is analogous to the pair maleate–fumarate (page 573), where, however, the dipole moments are not



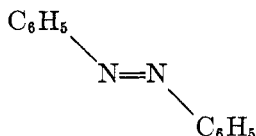
as different as in the above case.

It may finally be mentioned that in an analogous way the configuration of appropriate ethylene oxide derivatives can be determined. Bergmann and Schuetz (28) have compared the two isomeric 4,4'-dinitrostilbene oxides; their moments, 5.75 and 2.1, show that the former compound (m.p. 153–154°C.) has the *cis*-structure (with regard to the relative positions of the nitrophenyl groups), and that the other one (m.p. 200–201°C.) has the *trans*-configuration. In the latter case the moment is expectedly close to that of the unsubstituted ethylene oxide ( $\mu = 1.88$ ) (168) or stilbene oxide ( $\mu = 1.73$ ) (28). In this series, the method is still capable of wider application, as the various 4'-substituted 4-nitrostilbene oxides are easily accessible according to a method worked out by Bergmann and Hervey (25).

#### V. THE N=N DOUBLE BOND

The case of the azo compounds is completely analogous to that of the ethylenes, azobenzene itself having no dipole moment (23). In view of the fact that the N—C<sub>6</sub>H<sub>5</sub> valencies form an angle with the azo bond, and in view of the second observation that 4,4'-dibromoazobenzene and 4,4'-dimethylazobenzene (92) have no finite moment, one must assume that

these substances have the *trans*-configuration.<sup>22</sup> The same follows from



the fact that *p*-chloroazobenzene (23), *p*-bromoazobenzene (23), and *p*-methoxyazobenzene (31, 189) have the same dipole moment as the corresponding benzene derivatives. Recently, the *syn*-isomer of azobenzene has been discovered (91) and it has been shown to possess a distinct dipole moment, namely, 3.0 (92). This substance is photochemically reconverted into the stable isomer, and the interconversion can easily be followed by measuring

TABLE 6

SUBSTANCE	$\mu$
Diazoaminobenzene.....	0.90
4,4'-Dichlorodiazoaminobenzene.....	1.94
4,4'-Dibromodiazoaminobenzene.....	1.88
4-Bromodiazoaminobenzene.....	2.00
4-Nitrodiazoaminobenzene.....	4.17
4,4'-Dimethyldiazoaminobenzene.....	0.90
<i>N</i> -Methyldiazoaminobenzene.....	1.48
4,4'-Dibromo- <i>N</i> -methyldiazoaminobenzene.....	2.52

the change in dipole moment with time. (For other physical properties, see Cook, Jones, and Polya (56) and Corrucini and Gilbert (58).) In the case of *trans*-4,4'-dimethylazobenzene and other related compounds, dielectric measurements have shown that light also converts them gradually into the polar *cis*-forms (55).

Le Fèvre and Vine (114) have also made it apparent that the diazoamino compounds possess the *trans*-configuration (table 6).

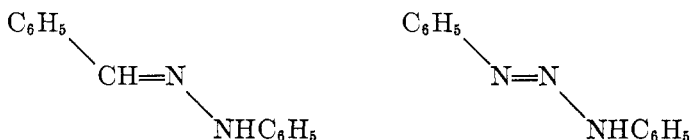
The angle,  $\Theta$ , at which the two phenyl groups are mutually inclined is about  $140^\circ$ . From the fact that substitution by chlorine in the two 4-positions increases the moment from 0.94 to 1.94, it follows that the two C—Cl vectors (1.55) produce a moment of  $1.94 + 0.90$  or of  $1.94 - 0.90$ . One obtains

$$\begin{array}{ll} (a) \quad 1.94 + 0.90 = 2 \times 1.55 \cos \Theta/2; & \Theta = 47.5^\circ \\ (b) \quad 1.94 - 0.90 = 2 \times 1.55 \cos \Theta/2; & \Theta = 140^\circ \end{array}$$

The former solution, however, is highly improbable and is, moreover, in disagreement with the fact that substitution by two methyl groups in the 4-positions does not affect the moment of diazoaminobenzene.

<sup>22</sup> Since stilbene and azobenzene give mixed crystals, stilbene must also be a *trans*-compound as, without experimental proof, has always been tacitly assumed. For the x-ray structure of crystalline stilbene, see reference 138 and compare reference 134.

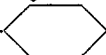

For diazoaminobenzene the same conclusion has been drawn previously by Ciusa and Pestalozza (54) from the observation that it gives mixed crystals with the *anti*-form of benzaldehyde phenylhydrazone.



Another group of azo compounds to which the method of dipole moments can be applied are the diazocyanides  $\text{ArN}=\text{NCN}$  (113) (see table 7). The *trans*-forms in this case should always have the highest moment, with the exception of the nitro compounds, since Le Fèvre and Vine (113) have

TABLE 7

SUBSTANCE	CONFIGURATION	$\mu$
4-Chlorophenyldiazocyanide.....	<i>Cis</i>	2.93
	<i>Trans</i>	3.73
4-Bromophenyldiazocyanide.....	<i>Cis</i>	2.91
	<i>Trans</i>	3.78
2-Bromophenyldiazocyanide.....	<i>Cis</i>	3.79
	<i>Trans</i>	5.32
4-Nitrophenyldiazocyanide.....	<i>Cis</i>	2.04
	<i>Trans</i>	1.47
2,4,6-Tribromophenyldiazocyanide.....	<i>Cis</i>	2.5
	<i>Trans</i>	4.0

shown that the N—CN moment will always be directed away from the azo group, as is the case with the  $\text{NO}_2$ ——N moment, while the Hal——N moment is, although small, directed towards the azo link. The similarity of these substances to the azo compounds proper follows from the observation (156) that their *trans*-forms are also converted photochemically into the *syn*-isomers.

In this series no more fundamentally new discoveries are to be expected; it may only be added that azomethane also has a dipole moment of 0 and therefore has the *trans*-configuration (199), a conclusion which is supported by the investigation of electron diffraction by gaseous azomethane (40).

#### VI. THE C=N DOUBLE BOND

The evaluation of the dipole moments of C=N compounds, even the most favorable ones, is hampered by the fact that, in contradistinction to

the C=C and the N=N double bonds, the C=N group in itself possesses a dipole moment. The only very clear-cut case, therefore, in this group, is that of carbodianil (compare 24),  $C_6H_5N=C=NC_6H_5$ , in which the two C=N moments cancel each other. According to E. Bergmann and W. Schuetz (27), its moment is 1.89 (that of the 4,4'-dimethyl derivative is 1.96). The structure of carbodianil resembles that of tetraphenylallene. Its moment is due to the fact that the two polar bonds ( $N-C_6H_5$ ) lie in two planes perpendicular to each other and is connected with the con-

TABLE 8\*†

SUBSTANCE	$\mu$	REFERENCE
(Benzaldehyde anil) . . . . .	1.57	(59)
4-Chlorobenzaldehyde anil . . . . .	1.77	(59)
4-Chlorobenzaldehyde 4'-methylanil . . . . .	2.06	(59)
4-Chlorobenzaldehyde 4'-chloroanil . . . . .	1.56	(59)
(Benzophenone anil) . . . . .	1.96	(21, 86)
(Benzophenone 4''-chloroanil) . . . . .	2.93	(21, 86)
4-Chlorobenzophenone anil . . . . .	1.95	(86)
4-Chlorobenzophenone 4''-chloroanil . . . . .	2.49	(86)
(4,4'-Dichlorobenzophenone anil) . . . . .	0.97	(86)
(Benzophenone chloroimine) . . . . .	2.96	(175)
(Benzophenone bromoimine) . . . . .	2.83	(175)
$\alpha$ -4-Chlorobenzophenone chloroimine . . . . .	2.47	(175)
$\beta$ -4-Chlorobenzophenone chloroimine . . . . .	2.67	(175)

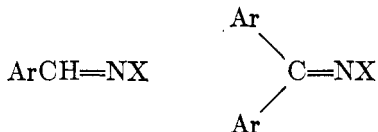
\* The complication brought about by the bent nature of the OH and OR groups is so great that salicylideneaniline ( $\mu = 2.45$ ), 5-bromosalicylideneaniline ( $\mu = 1.12$ ), salicylidene-*m*-toluidine ( $\mu = 2.59$ ), and 2-methoxybenzylideneaniline ( $\mu = 3.02$ ) mentioned by de Gaouck and Le Fèvre (59) will not be discussed here and therefore are not included in table 8. The same applies to *p*-homosalicylideneaniline and ethyl salicylidene-*p*-aminobenzoate (60).

† The substances in brackets either gave no stereoisomeric forms, or their structure cannot be defined by evaluation of the dipole moment.

figuration of the molecule by the same formula as for tetraphenylallene (page 574). Assuming the  $N-C_6H_5$  moment to be 1.34 (173), and that the angle between the C=N and the  $N-C_6H_5$  bond is  $120^\circ$ ,—corresponding to the valency angle in the allene molecule,—the moment of carbodianil should be 1.64. The difference may be due to inexactness of the assumptions made.

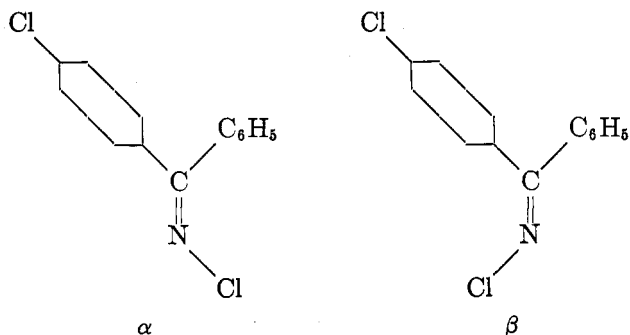
Benzalazine,  $C_6H_5CH=N-N=CHC_6H_5$ , also seems to be a simple case, but, as has been pointed out by Sutton (173), three *trans*-structures are possible, only one of them being polar. The significance of the slight dipole moment (0.89 (96); 1.00, 1.04 (182)) is therefore uncertain.

A second, less simple case is that of the benzaldehyde imines and benzophenone imines:

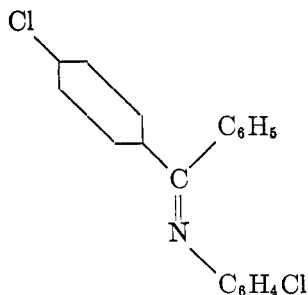


The experimental material available is summarized in table 8.

The difference in moment between the last two substances, although small, is most probably due to different configurations, the  $\alpha$ -compound having the chlorine atoms on different sides relative to the C=N plane.



The smallness of the difference is due to the smallness of the nitrogen-halogen moments, as pointed out by Theilacker and Fauser (175). It is further obvious that 4-chlorobenzophenone 4''-chloroanil must also be the *trans*-compound (corresponding to  $\alpha$ ),



as its moment is identical with that of  $\alpha$ -4-chlorobenzophenone chloroimine. That, as would be expected, the interposition of the phenyl between nitrogen and chlorine is of no influence, follows also from the identity in the moments of benzophenone 4''-chloroanil and benzophenone chloroimine.

Since in the other cases no stereoisomeric forms are known, the assignment of a configurational formula is more difficult. If  $\nu$  is the value of the  $C_6H_5-N$  moment, and  $\alpha$  the angle between  $\nu$  and the moment  $\xi$  of the  $C=N$  bond, then these data are connected with the moment,  $\mu$ , of benzophenone anil by the formula

$$\mu^2 = \nu^2 + \xi^2 - 2\nu\xi \cos (180 - \alpha)$$

If we assume  $\nu$  to be  $-1.34$  and  $\alpha$  to be  $120^\circ$ , we obtain

$$\mu^2 = 1.34^2 + \xi^2 - 1.34\xi$$

and with  $\mu = 1.97$ ,  $\xi = 2.27$ .

Following a calculation made by Theilacker and Fauser, the moment of the *trans*- and the *cis*-forms ( $y$ ,  $z$ ) of 4-chlorobenzophenone anil would then be given by the following formulas:

$$y^2 = \mu_{Cl}^2 + \xi^2 + \nu^2 - \xi\mu_{Cl} + \nu\xi - 2\nu\mu_{Cl}$$

$$z^2 = \mu_{Cl}^2 + \xi^2 + \nu^2 - \xi\mu_{Cl} + \nu\xi + \nu\mu_{Cl}$$

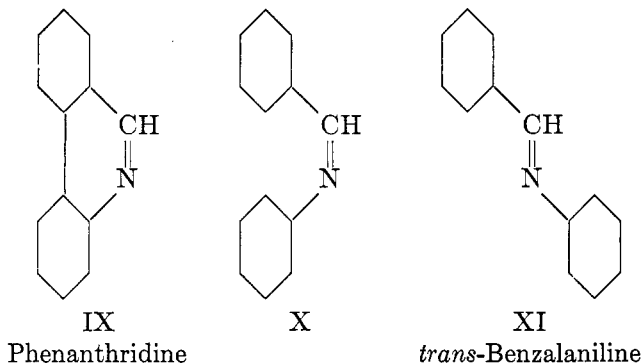
$$y = 2.6; z = 0.9$$

4-Chlorobenzophenone anil ( $\mu = 1.95$ ) is therefore the *trans*-compound. The *trans*-compound should have the higher moment, as the direction of the  $N-C_6H_5$  moment is not opposite to that of the  $C-Cl$  bond.

With regard to the benzaldehyde derivatives, it is difficult to understand at first glance why they have so much lower dipole moments than the corresponding benzophenone derivatives, and one would come to think that they all are *cis*(*syn*)-compounds. As, however, the dipole moments of benzylideneaniline and of 4-chlorobenzylidene-4'-chloroaniline are essentially identical, one must assume that both these substances are *trans*-compounds, and the same will apply to other representatives of this series.

The apparent discrepancy between the anils of benzophenone and benzaldehyde may be explained by the assumption that the valency angles at the doubly linked carbon atom are not identical in both cases, the distribution in the case of two phenyl substituents being probably more regular. A similar reasoning may apply to the recent observation of de Gaouck and Le Fèvre (60) that phenanthridine (IX), which may be regarded as analogous to the unknown *cis*-benzalaniline (X), has in fact the same dipole moment as *trans*-benzalaniline (XI).

It may be recalled in this connection that, in general, the Raman frequencies of the  $C=N$  double bond coincide with those of the *trans*-ethylenic system.

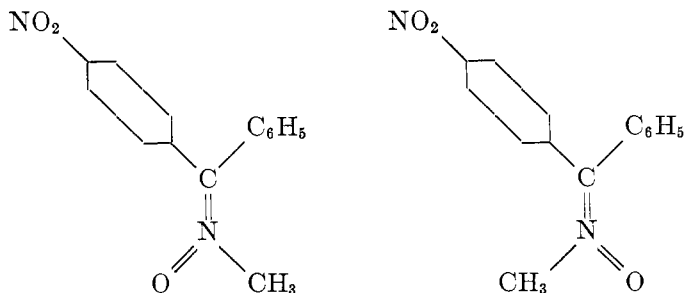


A still more complicated case is that of the oximes and phenylhydrazones, where by the oxygen and the imino nitrogen a new factor of uncertainty is introduced into the calculation. As a matter of fact, only the comparison of isomeric pairs can lead to success here and, in the hands of Sutton and Taylor (174), has already done so (table 9).

TABLE 9

SUBSTANCE	$\mu$
4-Nitrobenzophenone $\alpha$ -oxime <i>N</i> -methyl ether.....	6.60
4-Nitrobenzophenone $\beta$ -oxime <i>N</i> -methyl ether.....	1.09
4-Nitrobenzophenone $\alpha$ -oxime <i>O</i> -methyl ether.....	3.75
4-Nitrobenzophenone $\beta$ -oxime <i>O</i> -methyl ether.....	4.26
4-Nitrobenzaldehyde $\beta$ -oxime <i>N</i> -methyl ether.....	6.40
4-Nitrobenzaldehyde $\alpha$ -oxime <i>O</i> -methyl ether.....	3.40
4-Nitrobenzaldehyde $\beta$ -oxime <i>O</i> -methyl ether.....	3.89

It becomes clear at once that the  $\alpha$ - and  $\beta$ -compounds in both series correspond to each other, and an inspection of the formulas for the *N*-methyl ethers shows that the compound with the low moment must have



the  $\text{—NO}_2$  and the  $\text{=O}$  groups on different sides of the  $\text{C=N}$  double bond.



For the *O*-methyl ethers, the correlation between dipole moment and the molecular architecture cannot be derived, for reasons given above. But as for the 4-nitrobenzophenone oximes the configuration is known through the *N*-methyl ethers, and the same applies to the *O*-methyl compounds, so that the parallelism between the conditions in the benzophenone and the benzaldehyde series is a sufficient indication as to the structure of the isomeric benzaldoximes. How difficult the conditions may become is evident from the moments observed by Parsons and Porter (133) for the isomeric oximes of the three chlorobenzophenones (table 10). It would be expected that—at least in the *para* series—the difference would be as great as for the 4-nitrobenzophenone oxime *O*-methyl ethers and would lie in the same direction, but apparently the presence of the free hydroxyl groups, which would cause association (and in the different cases to a different extent), effaces the influence of the configurational factors.

Nevertheless, the experiments of Sutton and Taylor have shown that measurements of dipole moments will give a valuable lead towards elucidating the configurational relationships in the oxime series and they have given final support to Meisenheimer's (127) thesis that in the Beckmann rearrangement of oximes exchange of *trans*-substituents takes place, e.g.,

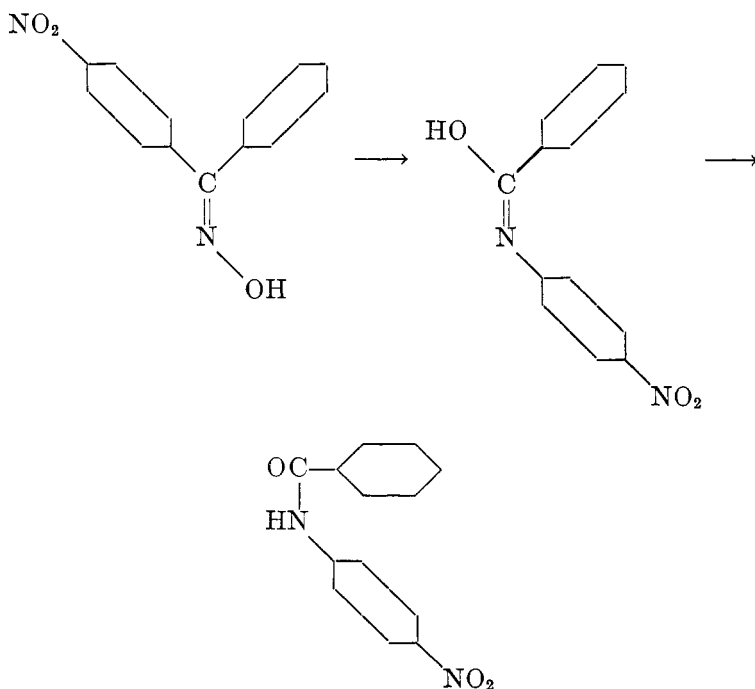
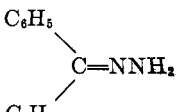
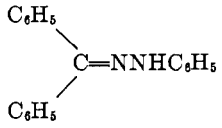
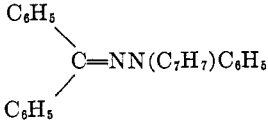
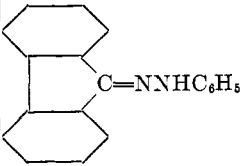
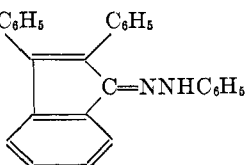


TABLE 10

SUBSTANCE	$\mu$
$\alpha$ -2-Chlorobenzophenone oxime.....	1.61
$\beta$ -2-Chlorobenzophenone oxime.....	1.61
$\alpha$ -3-Chlorobenzophenone oxime.....	1.50
$\beta$ -3-Chlorobenzophenone oxime.....	1.61
$\alpha$ -4-Chlorobenzophenone oxime.....	2.32
$\beta$ -4-Chlorobenzophenone oxime.....	2.38

TABLE 11

SUBSTANCE	FORMULA	$\mu$	REFER- ENCE
Benzophenone hydrazone.....		2.02	(32)
Benzophenone phenylhydrazone.....		2.22	(32)
Benzophenone benzylphenylhydrazone.....		2.60	(32)
Fluorenone phenylhydrazone.....		2.12	(32)
2,3-Diphenylindone phenylhydrazone.....		1.93	(32)
Benzaldehyde phenylhydrazone.....	$C_6H_5CH=NNHC_6H_5$	2.06	(182)
$\alpha$ -Nitroformaldehyde phenylhydrazone.....	$NO_2CH=NNHC_6H_5$	3.34	(102)
$\alpha$ -Acetaldehyde phenylhydrazone.....	$CH_3CH=NNHC_6H_5$	2.61	(102)
$\beta$ -Acetaldehyde phenylhydrazone.....	$(CH_3)_2C=NNHC_6H_5$	2.58	(102)
Acetone phenylhydrazone.....	$(CH_3)_2C=NNHC_6H_5$	2.68	(102)
$\alpha$ -Benzoylformaldehyde phenylhydrazone.....	$C_6H_5COCH=NNHC_6H_5$	1.70	(102)
$\beta$ -Benzoylformaldehyde phenylhydrazone.....	$C_6H_5COCH=NNHC_6H_5$	2.72	(102)

It would therefore be interesting to use this method also for the oximes of substituted benzalacetophenones and cinnamaldehydes. A discussion of the prevailing relationships by Auwers and coworkers from one side (5, 6, 8) and Blatt from the other side (37, 38) has brought no final decision, which is all the more to be desired, as, on the basis of the pertaining facts, Auwers still raises some doubt as to the general validity of Meisenheimer's theory.

TABLE 12

$c$	$\rho$	$\epsilon$	$n^2$	$P_{\frac{1}{2}}$	$PE_{\frac{1}{2}}$	$P$	$P_E$	$P_{A+O}$	$P_{A+O}^{\infty}$	$\mu$
4,4'-Dimethoxyisostilbene; $t = 16.0^\circ\text{C.}$ ; in benzene										
0	0.8834	2.2920	2.2920	26.579	26.579			→		
0.01415	0.8911	2.3733	2.3106	28.294	27.395	147.81	84.23	63.58		
0.01917	0.8938	2.4014	2.3178	28.891	27.694	147.16	84.72	62.44	66.9	1.77
0.02393	0.8964	2.4262	2.3239	28.430	27.966	145.73	84.51	61.22		
0.02792	0.8986	2.4507	2.3287	29.933	28.188	146.70	84.18	62.52		
4-Aminodiphenyl; $t = 21.8^\circ\text{C.}$ ; in benzene										
0	0.8765	2.2803	2.2803	26.618	26.618			→		
0.01848	0.8830	2.3774	2.3037	28.396	27.341	122.87	63.18	59.69		
0.02819	0.8864	2.4290	2.3106	29.327	27.636	122.72	62.73	59.99	61.0	1.71
0.03418	0.8884	2.4554	2.3179	29.382	27.865	120.36	63.13	57.23		
0.04504	0.8932	2.5192	2.3316	30.933	28.287	122.43	63.68	58.75		
2-Bromo-6-nitronaphthalene; $t = 20.4^\circ\text{C.}$ ; in benzene										
0	0.8782	2.2817	2.2817	26.588	26.588			→		
0.00352	0.8831	2.3078	2.2866	27.312	26.719	232.14	63.82	168.32		
0.00490	0.8850	2.3468	2.2883	27.606	26.767	234.48	63.20	171.28	172.7	2.87
0.00597	0.8865	2.3632	2.2892	27.854	26.798	238.81	61.75	174.06		
0.00730	0.8884	2.3608		28.124		236.95		174.03		
2-Nitro-3,5-dimethylbromobenzene; $t = 23.0^\circ\text{C.}$										
0	0.8751	2.2779	2.2430	26.626	26.111			→		
0.00287	0.8789	2.3691	2.2440	27.969	26.162	494.57	44.02	450.55		
0.00626	0.8833	2.4337	2.2464	28.912	26.244	391.90	47.43	344.47	334.2	4.00
0.00393	0.8802	2.3688		27.978		371.25	(47.43)	323.82	(average)	

In table 11 a number of phenylhydrazones have been listed; some of them have been discussed by Jensen and Bak (102) without any final decision as to their configuration.

## VII. APPENDIX

In this appendix are reproduced a few dipole moment data which have not been published previously and to which reference has been made in the preceding pages.

### A. Substances

4,4'-Dimethoxyisostilbene (m.p. 35°C.) was prepared according to the method given by Schlenk and Bergmann (145). Prepared according to Schlenk (143), 4-aminodiphenyl melts at 51°C. For 2-nitro-3,5-dimethylbromobenzene, the data are given in note 2, while 2-bromo-6-nitronaphthalene was obtained by the following procedure: 13 g. of 6-nitro-2-naphthylamine (1) was dissolved in concentrated sulfuric acid, the solution was poured into ice (80 g.) and was then diazotized with sodium nitrite (5 g.). To this solution a warm (40°C.) solution of sodium bromocuprite was added (from 27 g. of copper sulfate, 75 g. of sodium bromide, and 7 g. of copper bronze in 200 cc. of water), and the solid reaction product was filtered off, dried, and thoroughly extracted with ether. The ether residue was first distilled *in vacuo* and was then recrystallized from glacial acetic acid. The yield was 10 per cent, and the substance melted at 191°C. (Calculated for  $C_{10}H_6O_2NBr$ : C, 47.6 per cent; H, 2.4 per cent. Found: C, 47.8 per cent; H, 2.6 per cent.)

### B. Measurements

The figures in table 12 have the following significance:  $c$ , molar fraction;  $\rho$ , density;  $\epsilon$ , dielectric constant;  $n$ , refractive index;  $P_{\frac{1}{2}}$ , total polarization ( $P_{E\frac{1}{2}}$ , electronic polarization) for the solution;  $P(P_E)$  the same for the solute;  $P_{A+O}$ , atomic and orientation polarization, which is extrapolated graphically to infinite dilution ( $P_{A+O}^{\infty}$ ).

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