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STUDIORUM PROGRESSUS

The Labile Stereochemistry of Conjugated Systems[1]

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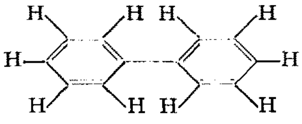
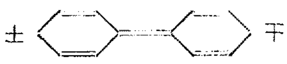
Classical conjugated systems, i.e. those containing alternating single and multiple bonds, have long occupied a prominent place in Organic Chemistry, both for their factual importance and their theoretical interest. Although the stereochemistry of such systems has been extensively studied, it is only in the case of simple benzenoid compounds, however, that the disposition of the atoms in space may be claimed to have been fully elucidated. The quantitative solution of this problem was achieved by the methods of X-ray and electron diffraction, and of ultraviolet and infrared spectroscopy, and was greatly facilitated by the flatness, symmetry and rigidity of the benzene molecule and many of its derivatives.

Other conjugated systems present considerably greater difficulties to precise analysis for several reasons. The most important of these is that, whereas benzenoid systems approach in varying degrees the state of "perfect" conjugation which exists in benzene itself and in which all the conjugated bonds posses the same amount of double-bond character, electronic interaction in other types of conjugated systems is usually far less complete, so that we must distinguish between bonds essentially single and essentially double (or triple) in character. The stereochemistry of partly benzenoid and non-benzenoid conjugated systems therefore consists of two separate, though inter-related parts, that of the single and that of the multiple bonds. Much progress has recently been made with both these aspects, but this article will be concerned mainly with the first–the stereochemistry of the conventional single bonds.

Diphenyl. The spatial arrangement of groups about single bonds (conformation) is generally much more labile than about double bonds (configuration) and the restrictions to free rotation arise from quite different causes. In the case of double bonds, they arise mainly from attractional forces between the unsaturation electrons which normally provide energy barriers exceeding 20 kcal/mol and result in stable geometrical isomers. In the case of "pure" single bonds, on the other hand, the restrictions are due to repulsional forces between non-bonded atoms which normally amount to less than 10 kcal/mol, so that the different conformations are readily interconvertible at ordinary temperatures and cannot be studied by methods requiring their chemical isolation. In the hybrid bonds present in conjugated systems, both factors may come into play. This is the case, for example, in diphenyl (I); π electronic forces will tend to render the molecule uniplanar in order to permit maximum contributions from dipolar resonance structures such as (II) and maximum overlap of the π orbitals, whereas repulsion forces between the o-hydrogen atoms will tend to make the molecule non-planar.



(I)



(II)

The conformation of minimum potential energy will therefore have an interplanar angle Θ somewhere between 0° and 90°, but we cannot accurately predict its value because we have no precise data for either the maximum resonance energy or the maximum repulsion energy, and we know even less about the variation of these quantities with Θ. However, in this particular case, we might expect that the resonance energy (ca. 5 kcal/mol) will exceed the repulsion energy between the rather small hydrogen atoms, and therefore that Θ will be nearer 0° than 90°. The actual angle has been reported to be about 0° in the crystalline state[1] (where additional, intermolecular forces come into play), but 45° in the vapour phase[2]. Some doubts have been expressed about both these values, but it is reasonable to assume that diphenyl is near-planar ($\Theta < 20°$) in solution at ordinary temperatures.

The replacement of o-hydrogen atoms by larger groups will increase the repulsion forces and therefore Θ, but, as is well-known, two or more o-substituents are usually required, unless they are of exceptional size, to restrict rotation sufficiently for the existence of resolvable, optically active isomers of reasonable life-time in an asymmetric diphenyl[3]. Thus, the classical chemical method of optical resolution provides a test of the energy barrier to rotation, rather than of the extent of non-planarity in the stable conformations, and represents a relatively crude weapon in investigating the stereochemistry about single bonds. For further progress we must turn to physical methods, most of which yield information about molecular structure in its equilibrium state. Unfortunately, the most precise methods, such as X-ray and electron diffraction are, at present, largely restricted to the solid and gas phase, respectively, and are inapplicable to the study of molecules in solution–i.e. to conditions of particular interest to the chemist. An analytically less precise but experimentally simpler method, which is not subject to this limitation, is absorption spectroscopy. Electronic spectra, in particular, afford a very sensitive index of steric effects in conjugated systems, and make it possible to obtain at least semi-quantitative information concerning interplanar angles.

Ortho-Substituted Diphenyls. One reason why ultraviolet and visible spectral properties are especially sensitive to steric effects is that they are conditioned by differences between the ground state and electronically excited states, and that the steric requirements of the latter are often considerably more exacting than those of the ground state. This is true for example of the 2510Å-band (K-band) of diphenyl, which may be regarded as due to a transition from a ground state in which dipolar structures such as (II) make relatively small contributions, to an excited state in which such structures make relatively large contributions. The introductions of o-substituents, which cause severe

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[1] Summary of a lecture delivered at the Eidgenössische Technische Hochschule, Zürich, on January 24, 1955.

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[1] J. DHAR, Proc. Nat. Inst. Sci. India *15*, 11 (1949).

[2] O. BASTIANSEN, Acta Chem. Scand. *3*, 408 (1949).

[3] See R. ADAMS and H. C. YUAN, Chem. Reviews *12*, 261 (1933).

hindrance and prevent uniplanarity, will obviously affect the excited state more than the ground state and will raise the energy level of the former with respect to the latter; i.e. the transition energy increases and the K-band is displaced to shorter wave-length. If the steric repulsion is sufficiently great and equals or exceeds the resonance stabilisation, the interplanar angle in the ground state will approach 90° and the two benzene rings will become electronically independent; i.e. the absorption of the system will revert to that of the two separate chromophores. Such phenomena were first observed with the *o*-methyldiphenyls[1]. The K-Band is shifted to 2350 Å in 2-methyldiphenyl, and to ca. 2150 Å in 2:2′-dimethyldiphenyl, and disappears completely in 2:2′:6:6′-tetramethyldiphenyl. From the spectral data, it is possible to construct an energy level diagram (Fig. 1). The resonance stabilisation in the ground state of diphenyl is known from thermo-chemical data to be *ca.* 5 kcal/mol relative to benzene, and the resonance energy (RE) of the excited state can be deduced to be 34 kcal/mol. Since even one *o*-methyl substituent will cause steric repulsion exceeding 10 kcal/mol, the RE's for ground states of the mono-, di- and tetra-methyl derivatives will be almost nil, while the RE's of the excited states will be reduced to *ca.* 21, 10, and 0 kcal/mol, respectively. Although the exact function which connects RE with the interplanar angle is not known, we can make a rough estimate of Θ by using the simplest function which passes through the fixed points $\Theta = 0$ (maximum RE) and $\Theta = 90°$ (minimum RE), namely

$$\mathrm{RE} = k \cos^2 \Theta \qquad (1)$$

The values of Θ obtained in this way are *ca.* 40° for mono-, 60° for di-, and 90° for tetra-*o*-methyldiphenyl.

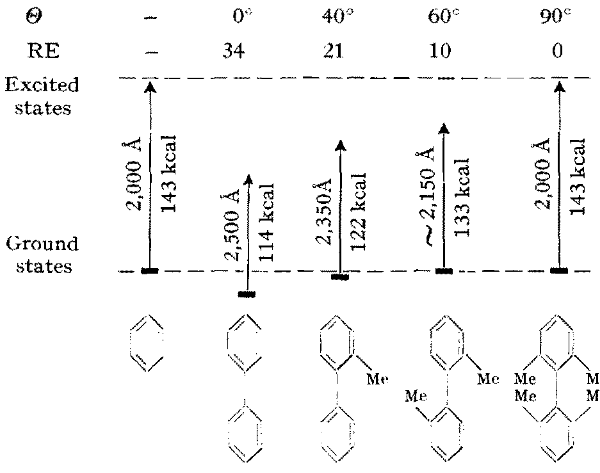

Fig. 1.–Electronic transitions between non-planar grounds states and non-planar excited states. (Energy level diagram for diphenyl and *ortho*-methyldiphenyls.)

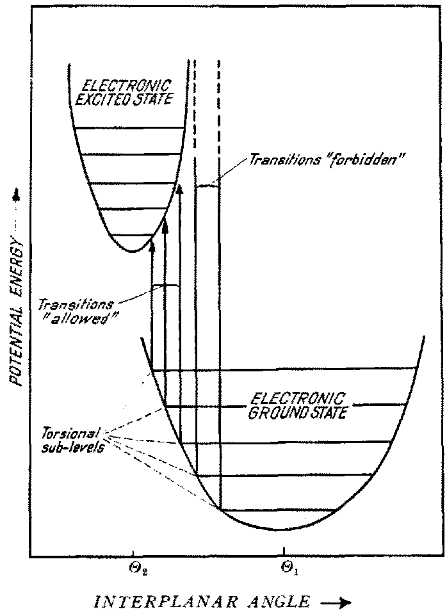

Fig.2.–Electronic transitions between non-planar ground states and near-planar excited states (potential energy curves).

Ortho-Bridged Diphenyls. A different kind of situation can arise if steric hindrance to uniplanarity is relatively small, either because the repulsion forces are weak or because they are compensated by bonding forces which tend to keep the system planar. A good example of the latter type is provided by *ortho*-bridged diphenyls such as 9:10-dihydrophenanthrene, dihydrodibenzoxepin and dihydrodibenzazepinium derivatives. The ultraviolet spectra of these compounds are quite different from those of *o*:*o*′-disubstituted diphenyls; the "diphenyl"-bands show the usual bathochromic, instead of hypsochromic, displacements and only the intensities are decreased as compared with diphenyl (table I). The absence of any unusual λ shifts (< 50 Å) means that the transition energy, and therefore the energy levels of the ground and excited states, are almost unchanged (< 3 kcal) by any steric effects, but the decrease in ε shows that the transition probability is reduced. According to classical theory, transition energy and probability are normally interdependent, and a change in ε without change in λ must therefore be due to a sterically conditioned change in selection rules: the transition has evidently become partly "forbidden". We can interpret this in the following way[1]. Let us call the mean interplanar angle Θ_1 in the ground state, and Θ_2 in the excited state. Since the amount of double bond character of the single bond joining the two conjugated groups, and the resonance energy are increased in the excited state (see above), Θ_2 will be rather smaller than Θ_1. Now it is a fundamental principle, formulated by FRANCK and CONDON, that since the motion of electrons is very much faster than that of atomic nuclei, interatomic distances (and therefore, interplanar angles) cannot change during an electronic transition; in other words, transitions can only occur along vertical lines in the potential energy diagram (Fig. 2). Hence a molecule with $\Theta = \Theta_1$ cannot pass directly into the equilibrium conformation of the excited state with $\Theta = \Theta_2$. Transitions will, however, be possible between higher vibrational sub-levels for which Θ is intermediate between Θ_1 and Θ_2. Now, the spacings of the torsional vibrational states of a polyatomic molecule

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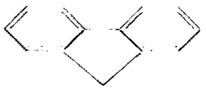
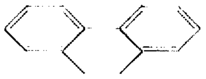
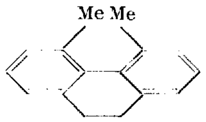
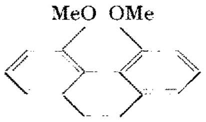
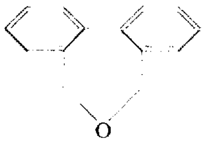
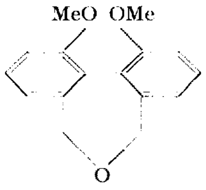
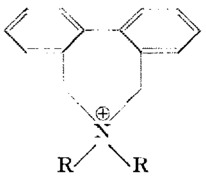
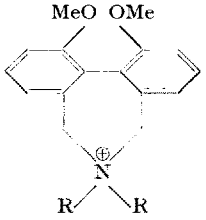
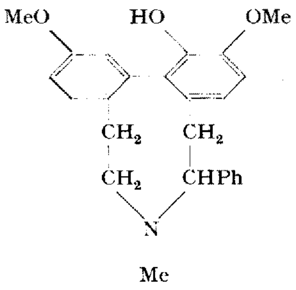
[1] L. W. PICKETT, G. F. WALTER, and H. FRANCE, J. Amer. Chem. Soc. *58*, 2296 (1936). – See E. A. BRAUDE and E. S. WAIGHT in "Progress in Stereochemistry" (W. KLYNE, Ed.), Vol. 1., Chapter 4 (Butterworths, London 1954), for a summary of data and literature references. – E. A. BRAUDE, F. SONDHEIMER, and W. F. FORBES, Nature *173*, 117 (1954), and forthcoming papers in J. Chem. Soc.

[1] E. A. BRAUDE, F. SONDHEIMER, and W. F. FORBES, Nature *173*, 117 (1954), and forthcoming papers in J. Chem. Soc.

Table I.–Ultraviolet Spectra (Diphenyl Bands) and Interplanar Angles of *ortho*-Bridged Diphenyls[1].

	$\lambda_{\max}$ Å	ε	$\varepsilon/\varepsilon_0$	Θ^0_1
	2,600	19,000	1·00	0
	2,640	17,000	0·90	18
	2,600	12,600	0·66	35
	2,720	13,500	0·71	32
	2,500	16,500	0·87	21
	2,530	8,700	0·46	47
	2,480	15,000	0·79	27
	2,375	11,500	0·61	39
	–	–	<0·1	>70

[1] Unless otherwise stated, the data in this and the following tables are taken from E. A. BRAUDE and E. S. WAIGHT, "Progress in Stereochemistry" (W. KLYNE, Ed.), Vol. 1., Chapter 4 (Butterworths, London, 1954), and E. A. BRAUDE, F. SONDHEIMER, and W. F. FORBES, Nature *173*, 117 (1954), and forthcoming papers in J. Chem. Soc.

are considerably closer than 3 kcal and the higher (i.e. non-equilibrium) states will be appreciably populated at ordinary temperatures, so that a fraction (r) of the molecules will have interplanar angles smaller than Θ_1 and sufficiently close to Θ_2 to be able to reach the excited state. As a first approximation, r will be given by $\varepsilon/\varepsilon_0$, where ε_0 is the value for the unsubstituted, planar parent compound and the simplest function connecting this with Θ_1 and Θ_2 is

$$r = \varepsilon/\varepsilon_0 = \cos^2(\Theta_1\text{-}\Theta_2) \qquad (2)$$

If we make the additional assumption (which will be justified later) that Θ_2 is almost zero, i.e. that the excited state is near-planar, this simplifies to[1]

$$\varepsilon/\varepsilon_0 = \cos^2\Theta_1 . \qquad (3)$$

The values for *ortho*-bridged diphenyls obtained in this way (using fluorene as reference compound) are given in table I. In the case of 9:10-dihydrophenanthrene and dihydrodibenzoxepin, the non-planarity of the phenyl rings is not due to non-bonded atom repulsions, but to the fairly rigid two-or three-atom bridge, and the angles deduced spectroscopically are in good agreement with those indicated by molecular models (Fig. 3). For the *o*-substituted derivatives, no reliable values can be obtained from static models since these do not indicate non-bonded repulsion forces, but the spectral data show that the increases in Θ_1 are relatively small, as might be expected since the conformation will still be determined mainly by the *ortho*-bridge. By contrast, phenyldihydrothebaine which contains a five-atom *ortho*-bridge, shows little diphenyl-type absorption; this is not surprising since in this case both the bridge and the other *ortho*-substituent will favour a highly noncoplanar arrangement of the benzene rings. The long-wavelength bands which are also shown by *ortho*-bridge diphenyls can be ascribed to hyperconjugative interaction of the phenyl groups through the bridge and to the usual auxochromic effects of substituents such as methoxyl. It should be mentioned, however, that a different interpretation has been put forward by TURNER and his colleagues[2], to whom we owe many of the spectral data just discussed.

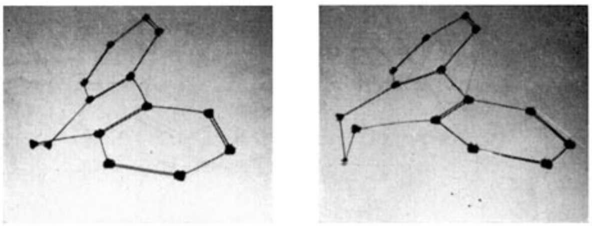


Fig. 3.–Molecular models of (*a*) 9:10-dihydrophenanthrene and (*b*) dibenzodihydroxepin.

We may thus distinguish between two different types of spectral steric effects[3]. The first, which results in

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[1] E. A. BRAUDE and E. S. WAIGHT, "Progress in Stereochemistry" (W. KLYNE, Ed.). Vol. 1., Chapter 4 (Butterworths, London 1954), and E. A. BRAUDE, F. SONDHEIMER, and W. F. FORBES, Nature *173*, 117 (1954) used a cos Θ function. The cos$^2\Theta$ function is more satisfactory because it has the value 1 for Θ = 0 and 180°, as well as from other theoretical considerations.

[2] G. H. BEAVEN, D. M. HALL, M. S. LESSLIE, and E. E. TURNER, J. Chem. Soc. *1952*, 854. – G. H. BEAVEN, D. M. HALL, M. S. LESSLIE, E. E. TURNER, and G. R. BIRD, J. Chem. Soc. *1954*, 131. – D. M HALL, S. RIDGWELL, and E. E. TURNER, J. Chem. Soc. *1954*, 2498.

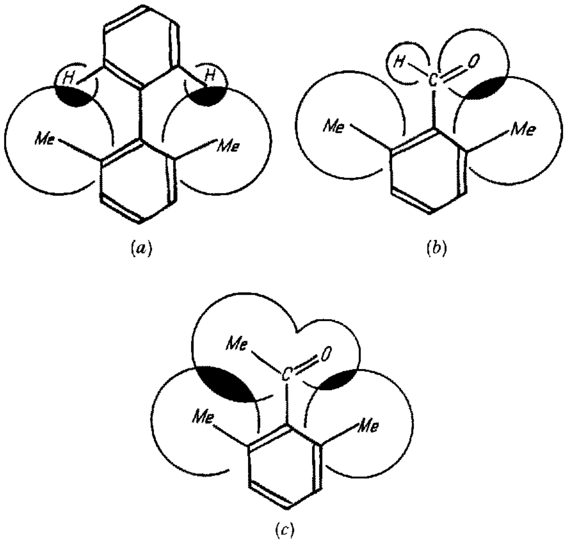
[3] E. A. BRAUDE, F. SONDHEIMER, and W. F. FORBES, Nature *173*, 117 (1954), and forthcoming papers in J. Chem. Soc.

hypsochromic shifts, involves transitions between non-planar ground states and non-planar excited states. The second, which results in no unusual wavelengths shifts but only in decrease in ε of the K-band, involves partly forbidden transitions between non-planar ground states and near-planar excited states. Only the latter type of effect allows us, at present, to deduce quantitative information concerning the stereochemistry of the conjugated system. Although this type of effect has only been recognized quite recently, it is already clear that it occurs very widely and the remainder of the article will be devoted to a discussion of some other interesting examples.

Table II.–Steric Effects in *ortho*-Substituted Benzaldehydes and Acetophenones

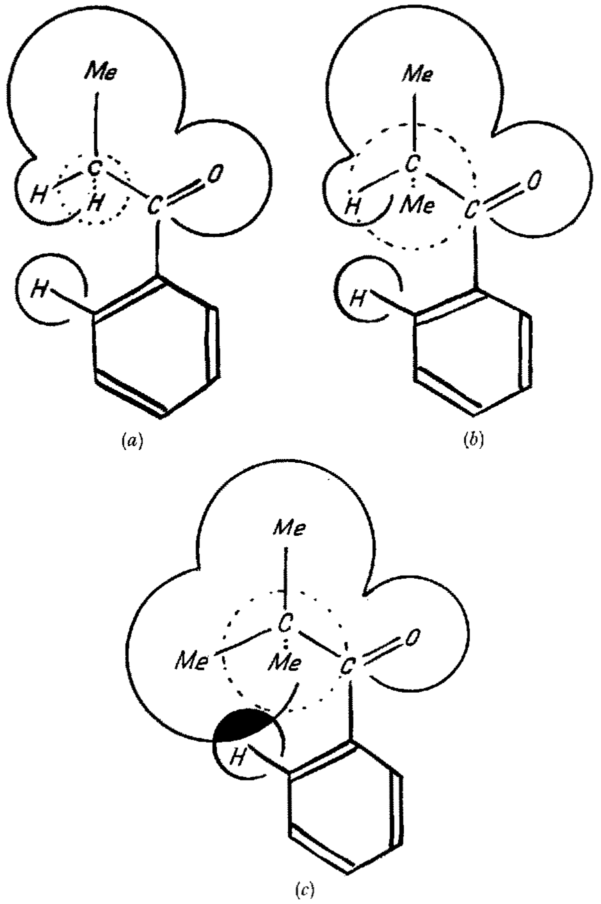
	$\lambda_{\mathrm{max.}}$, Å	ε	$\varepsilon/\varepsilon_0$	Θ_1^0
Benzaldehyde	2,420	14,000	1·00	0
4-Methyl-Benzaldehyde . . .	2,510	15,000	1·00	0
2-Methyl-Benzaldehyde . . .	2,510	13,000	0·87	21
2:6-Dimethyl-Benzaldehyde .	2,510	12,500	0·78	28
2:4:6-Trimethyl-Benzaldehyde	2,640	14,500	0·85	22
Acetophenone	2,420	13,000	1·00	0
4-Methyl-Acetophenone . . .	2,520	15,000	1·00	0
2-Methyl-Acetophenone . . .	2,420	8,500	0·58	40
2:4-Dimethyl-Acetophenone .	2,510	13,000	0·76	29
2:5-Dimethyl-Acetophenone .	2,450	10,000	0·59	39
2:6-Dimethyl-Acetophenone .	2,510	5,000	0·29	57
2:4:6-Trimethyl-Acetophenone	2,420	3,500	0·18	64

Aromatic ketones. A system which allows the comparison of interplanar angles deduced from electronic spectra with those given by another physical method are the *o*-alkylated benzaldehydes and acetophenones first studied by RODEBUSH[1]. The data in table II show that the K-bands, which are ascribed to a transition $\mathrm{Ph\text{-}C{=}O} \rightarrow {}^{+}\mathrm{Ph} = \mathrm{C\text{-}O^{-}}$, show only normal bathochromic shifts with alkylation, but that *o*-methyl groups produce a small decrease in ε in the aldehydes and a large decrease in ε in the ketones. (In the aldehydes, the effect only becomes apparent when the fact that methyl substituents normally produce a small *increase* in ε is taken into account.)[1] The reductions in intensity evidently arise from the non-planarity of the equilibrium conformation in the ground state, due to interference between the *o*-methyl and the formyl or acetyl groups, and the values of Θ_1 calculated by equation (3) are 20–30° for the aldehydes and 30–60° for the ketones. This is in agreement with scale-diagrams (Fig. 4), which indicate that steric overlap in the uniplanar conformation is negligible for the formyl-hydrogen atom, slight for the formyl- or acetyl-oxygen atom, but considerable for the acetyl-methyl group. It is also in agreement with the dipole moment measurements of SUTTON and his co-workers[2] which show that the mesomeric interaction between the phenyl and carbonyl groups is strongly reduced by *o*-methyl substituents. Now, dipole moments are a property of the electronic ground states alone and one can deduce Θ from the observed moment and the calculated moments for $\Theta_1 = 0$ and 90°, respectively. The values of Θ_1 obtained in this way are closely similar to, but slightly smaller than, those calculated from ε; the differences are almost certainly due to the fact that the "spectroscopic" angles really represent $(\Theta_1 - \Theta_2)$ (equation 2) instead of Θ_1 (equation 3). By substracting



(*a*) (*b*) (*c*)

Fig. 4.–Planar projections of (*a*) 2:6-methyldiphenyl, (*b*) 2:6-dimethylbenzaldehyde, (*c*) 2:6-dimethylacetophenone.



(*a*) (*b*) (*c*)

Fig. 5.–Planar projections of (*a*) phenyl ethyl ketone, (*b*) phenyl isopropyl ketone, (*c*) phenyl *tert.*-butyl ketone.

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[1] M. T. O'SHAUGHNESSY and W. H. RODEBUSH, J. Amer. Chem. Soc. *62*, 2906 (1940).

[1] E. A. BRAUDE, F. SONDHEIMER, and W. F. FORBES, Nature *173*, 117 (1954), and forthcoming papers in J. Chem. Soc.

[2] J. B. BENTLEY, K. B. EVERARD, R. J. B. MARSDEN, and L. E. SUTTON, J. Chem. Soc. *1949*, 2957.

the "dipole" angles from the "spectroscopic" angles, we thus get Θ_2; the values are quite small (10–15°) and therefore support our earlier conclusion that steric effects of this type involve near-planar excited states.

Table III.–Steric Effects in Phenyl Alkyl Ketones and Cyclic Aromatic Ketones

	$\lambda_{max.}$, Å	ε	$\varepsilon/\varepsilon_0$	Θ_1°
PhCOMe	2420	13200	1·0	0
PhCOEt	2420	13500	1·0	0
$PhCOC_5H_{11}$[a]	2380	12000	0·89	19
$PhCOCMe_3$[b, c]	2420	9100	0·68	34
$PhCOCMe_2Et$[d]	2390	8300	0·62	38
$PhCOCMeEt_2$[d]	2380	7100	0·53	43
1-Indanone[b, c]	2430	12300	0·91	17
1-Tetralone[b, c]	2480	11600	0·86	22
Benz*cyclo*heptan-1-one[e] . .	2460	8100	0·60	39
Benz*cyclo*octan-1-one[e] . .	2470	6500	0·48	46

[a] E. A. Braude and W. F. Forbes, J. Chem. Soc. *1951*, 1755.

[b] P. Ramart-Lucas, J. Hoch, and Mme Vial, Bull. Soc. Chim. France *1952*, 220.

[c] G. D. Hedden and W. G. Brown, J. Amer. Chem. Soc. *75*, 3744 (1953).

[d] D. J. Cram and J. D. Knight, J. Amer. Chem. Soc. *74*, 5839 (1952).

[e] R. Huisgen and W. Rapp, Ber. dtsch. chem. Ges. *85*, 836 (1952).

It will be noted that although the apparent extent of steric overlap is almost the same in *o*-methyldiphenyl and *o*-methylacetophenone (Fig. 4), the spectral consequences are quite different in the two systems. Hindrance to uniplanarity is evidently much less severe in the acetophenones, because the acetyl group is much more flexible than a phenyl group, so that the repulsion forces are much smaller. Steric effects similar to those shown by the acetophenones are observed, even in the absence of *ortho*-substituents, in phenyl *tert.*-alkyl ketones and in bicyclic ketones, such as tetralone (Table III). Whereas a primary or secondary alkyl group can adopt conformations involving little overlap with the *o*-hydrogen atoms of the phenyl ring, considerable interference is unavoidable in the case of a tertiary alkyl group (Fig. 5), resulting in interplanar angles of *ca.* 30°. In bicyclic ketones, on the other hand, non-planarity is mainly due not to interference with the phenyl ring, but to repulsions between the hydrogen atoms of the methylene groups, i.e. to the preferred pseudo-chair conformation of the alicyclic ring (Fig. 6).

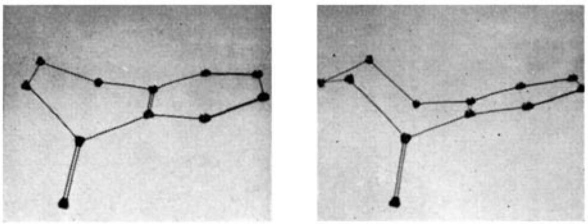


Fig. 6.–Molecular models of (*a*) α-tetralone, (*b*) benz*cyclo*heptan-1-one.

Styrenes. Since the valency angles at a double-bonded carbon atom tend to be the same (120°) whatever the other ligands, *ortho*-substituted styrenes might be expected to exhibit steric effects similar to those shown by acetophenones (Fig. 7). The data in table IV show that this is indeed the case. In *β*-substituted styrenes, the inter-planar angles show some dependence on the *β*-substituent; this is presumably because a conjugating group will affect the electronic forces which oppose non-planarity throughout the system, even though the group may not be directly involved in steric overlap.

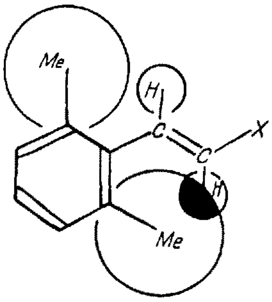


Fig. 7.–Planar projection of 2:6-dimethylstyrene derivative.

Table IV. – Steric Effects in *ortho*-Substituted Styrenes

X	=	H	CH = CH_2	CHMe·OH	COMe	CMe = N·$NHCONH_2$
PhCH=CHX	$\lambda_{max.}$ Å . . .	2,440[a]	2,800[c]	2,510[c]	2,860	3,050
	ε	14,000	28,300	19,500	22,200	38,600
$2\text{-}MeC_6H_4CH{=}CHX$	$\lambda_{max.}$ Å . . .	2,450[a]	2,810[c]	2,550[c]	2,900	3,040
	ε	12,600	25,000	16,000	17,000	32,500
	$\varepsilon/\varepsilon_0$	0·78	0·83	0·74	0·71	0·84
	Θ_1°	28	24	30	33	23
$2{:}6\text{-}Me_2C_6H_3{\cdot}CH{=}CHX$ . . .	$\lambda_{max.}$ Å . . .	—	—	—	2,910	2,820
	ε				10,500	23,300
	$\varepsilon/\varepsilon_0$				0·40	0·60
	Θ_1°				50	39
$2{:}4{:}6\text{-}Me_3C_6H_2CH{=}CHX$ . .	$\lambda_{max.}$ Å . . .	2,450[b]	—	2,510[d]	2,930[d]	—
	ε	7,000		7,500	14,000	
	$\varepsilon/\varepsilon_0$	0·35		0·29	0·50	
	Θ_1°	54		57	44	

[a] P. Ramart-Lucas and J. Hoch, Bull. Soc. chim. France *1935*, 327.

[b] K. C. Bryant, G. T. Kennedy, and E. M. Tanner, J. Chem. Soc. *1949*, 2389.

[c] E. A. Braude, E. R. H. Jones, and E. S. Stern, J. Chem. Soc. *1947*, 1087.

[d] K. R. Bharucha and B. C. L. Weedon, J. Chem. Soc. *1953*, 1571.

In 9-vinylanthracene derivatives, steric hindrance is much more severe than in 2:6-dimethylstyrene derivatives and hardly any conjugation between the aryl nucleus and the side-chain is apparent[1]. The difference undoubtedly arises from the greater rigidity in the polycyclic aromatic system of the 1:8-hydrogen atoms which are firmly held in an in-plane position (Fig. 8).

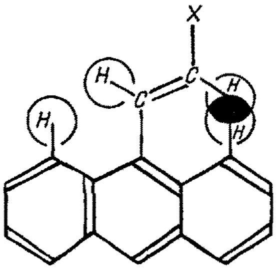


Fig. 8.–Planar projection of 9-vinylanthracene derivative.

Aromatic amines. All the examples discussed so far refer to classical or π–π conjugated systems. Strong interaction which may be termed π-p-conjugation, also occurs between multiple bonds and groups carrying unshared (p-) electron pairs. The steric requirements for maximum π-p-conjugation are that the π electron orbitals and p-electron orbitals should be parallel, i.e. that in an aromatic amine $ArNR_2$ the two groups R should lie in a plane parallel to that of the ring. Just as in acetophenones and styrenes, *o*-substituents will cause interference in the electronically optimum conformation (Fig. 9), and result in rotation about the Ar-N bond. The intensities of the K-bands, which are ascribable to the transition $Ar{-}NR_2 \rightarrow {}^{-}Ar{=}NR^{+}_2$, therefore decrease[2]; the interplanar angles calculated from the spectral data are similar to those deduced for comparable π–π conjugated systems (table V). In the bicyclic compound, TRÖGER's base (III), the angle between the planes of the phenyl rings and of the $-NR_2$ groups is fairly rigidly fixed[1]; the value shown by models ($\sim$ 45°) is in excellent agreement with that (43°) deduced from the ultraviolet spectra ($\lambda_{max.}$ 2500 Å, ε 8600). An extreme case of steric inhibition in an aromatic amine is presented by benzquinuclidine (IV); here the planes of the benzene ring and the $-NR_2$ groups are forced into almost perpendicular positions and no-K-band is observed[2].

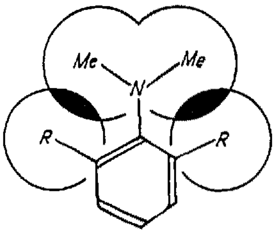
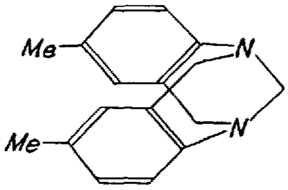


Fig. 9.–Planar projection of *ortho*-substituted *N*-dimethylaniline.

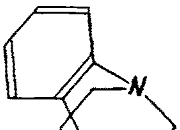
Table V.–Steric Effects in *ortho*-Substituted N-Dimethylanilines*

Substituent	$\lambda_{max.}$, Å	ε	$\varepsilon/\varepsilon_0$	Θ^0_1
None	2,500	14,000	1·00	0
2-Fluoro . . .	2,500	11,500	0·82	25
2-Chloro . . .	2,560	7,500	0·53	43
2-Bromo . . .	2,560	6,000	0·43	49
2-Methyl . . .	2,470	6,500	0·46	47
2-*tert.*-Butyl . .	–	< 1,000	< 0·1	>70
2:5-Dimethyl .	2,500	6,000	0·43	49
2:6-Dimethyl .	2,600	2,500	0·18	64

* Experimental data taken from W. R. REMINGTON, J. Amer. Chem. Soc. *67*, 1838 (1945); B. M. WEPSTER, Rec. Trav. Chim. Pays-Bas *72*, 662 (1953).

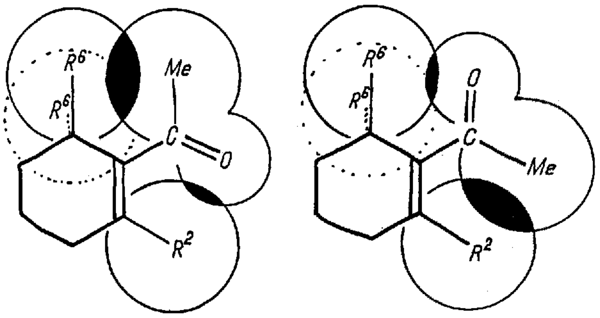


(III)



(IV)

cyclo*Hexene Derivatives.* The stereochemistry of non-benzenoid conjugated systems presents some additional problems. The K-bands and the geometries of the conjugated systems in *cyclo*hexene derivatives, such as 1-acetyl*cyclo*hexene and 1-vinyl*cyclo*hexene, resemble those of their benzenoid analogues, acetophenone and styrene, but unlike in the latter, the 2- and 6-positions are no longer equivalent and two different uniplanar conformations, *s-cis* and *s-trans*, are possible[3] (Fig. 10).



(*a*) (*b*)

Fig. 10.–Planar projections of (*a*) *s-cis* acetylcyclohexene and (*b*) *s-trans* acetyl*cyclo*hexene.

The planar *s-trans* conformation is electronically stabler by *ca.* 2–3 kcal than the *s-cis*, and in acetyl*cyclo*hexene a substituent will have a larger effect in the 2- than in the 6-position. This is borne out by the spectral data (table VI), but the decrease in ε in 1-acetyl-2-methyl-*cyclo*hexene could be due[4] either to a non-planar *s-trans* conformation or to a near-planar *s-cis* conformation, since ethylenic ketones with an enforced *cisoid* configuration show a similar decrease, which is ascribable to the reduced overall length of the chromophore and the smaller transition moment. Which conformation is favoured will obviously depend on the relative potentional energies. Since the absence of hypsochromic shifts

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[1] E. A. BRAUDE, J. S. FAWCETT, and D. D. E. NEWMAN, J. Chem. Soc. *1950*, 793.

[2] W. R. REMINGTON, J. Amer. Chem. Soc. *67*, 1838 (1945). – H. B. KLEVENS and J. R. PLATT, J. Amer. Chem. Soc. *71*, 1714 (1949).

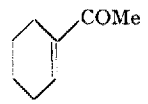
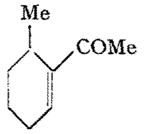
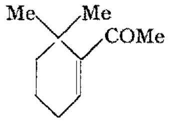
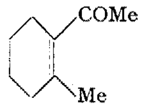
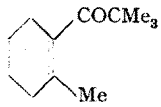
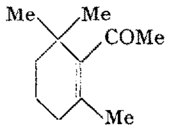
[1] V. PRELOG and P. WIELAND, Helv. Chim. Acta *27*, 1127 (1944).

[2] B. M. WEPSTER, Rec. Trav. Chim. Pays-Bas *72*, 662 (1953).

[3] E. A. BRAUDE, E. R. H. JONES, H. P. KOCH, R. W. RICHARDSON, F. SONDHEIMER, and B. J. TOOGOOD, J. Chem. Soc. *1949*, 1890.

[4] R. B. TURNER and D. M. VOITLE, J. Amer. Chem. Soc. *73*, 1403 (1951).

Table VI.–Ultraviolet Spectra ("K-bands"), Infrared Spectra ($C = O$ stretching frequencies) and Interplanar Angles of Substituted 1-Acetylcyclohexenes

	$\lambda_{\max.}$, Å	ε	$\varepsilon/\varepsilon_0$	Θ_1^0	ν, cm^{-1}	$\Delta\nu$, cm^{-1}
	2,320	12,500	1·0	0	1,665	42
	2,340	12,000[a]	0·96	11	–	–
	2,320	12,000	0·96	11	–	–
	2,450	6,500	0·52	44	1,678	29
	2,390	1,300[b]	0·10	71	1,684	17
	2,430	1,400	0·11	71	1,693	14

[a] E. A. BRAUDE and O. H. WHEELER, J. Chem. Soc. *1955*, 329.
[b] Unpublished experiments by Dr. C. J. TIMMONS.

implies that steric hindrance amounts to not more than 1 kcal, i.e. less than the extra resonance stabilisation in the *s-trans* conformation, it seems probable in the present case that a non-planar *s-trans* conformation ($\Theta_1 = 45°$) will be preferred to a near-planar *s-cis*-conformation ($\Theta_1 \sim 180°$). This is borne out by the parallelism between the effects of *o*-methyl substituents in the alicyclic and benzenoid ketones, not only with regard to the ultraviolet but also to the infrared or Raman spectral properties. Thus, the carbonyl stretching frequencies show a progressive decrease with increasing hindrance and approach the value for unconjugated ketones; an approximately linear relationship exists between Θ_1 and the ratio $\Delta\nu/\Delta\nu_0$ of the frequency shifts in the non-planar and planar compounds (Fig. 11). It will be noted that the consequence of non-planarity in vibrational spectra, unlike in electronic spectra, is a change in frequency (i.e. wavelength), indicating that the mechanical coupling which governs the former is a much more sensitive function of interplanar angle than electronic coupling, which governs the latter.

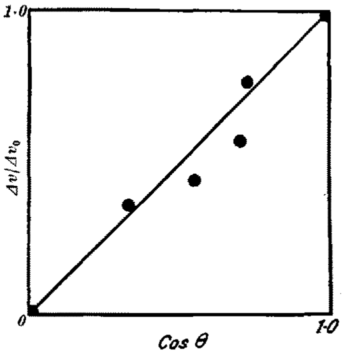
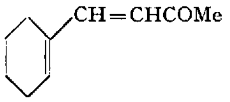
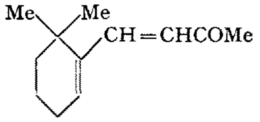
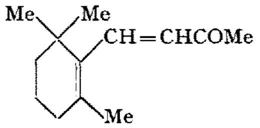
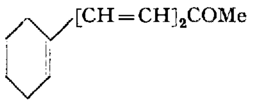
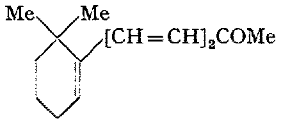
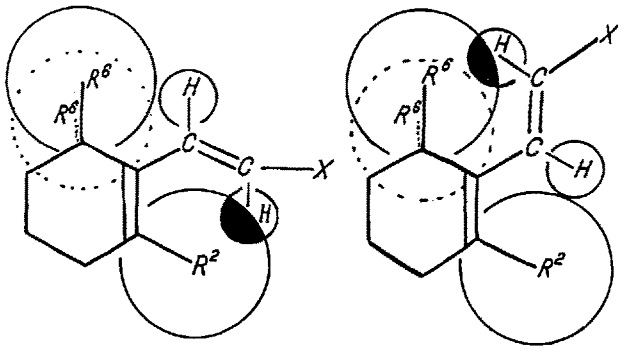


Fig. 11.–Plot of interplanar angle against relative carbonyl stretching frequency shifts for alicyclic and benzenoid ketones.

Table VII.–Steric Effects in 1-Vinylcyclohexene Derivatives

	$\lambda_{\max.}$, Å	ε	$\varepsilon/\varepsilon_0$	Θ_1^0
	2,810	20,800	1·0	0
	2,810	13,000	0·65	36
	2,960	10,700	0·46	47
	3,200	37,500	1·0	0
	3,260	15,500	0·41	50



(*a*) (*b*)

Fig. 12.–Planar projection of (*a*) *s-cis* vinyl*cyclo*hexene and (*b*) *s-trans*vinyl*cyclo*hexene derivatives.

In 1-vinyl*cyclo*hexenes, the relative effects of 2- and 6-substituents will be reversed, the latter being sterically more effective in the *s-trans* conformation (Fig. 12). This is well illustrated by data for the dienones of the β-ionone type[1] (table VII). The fact that the non-planar *s-trans* conformation is preferred in such systems, even though

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[1] E. A. BRAUDE, E. R. H. JONES, H. P. KOCH, R. W. RICHARDSON, F. SONDHEIMER, and J. B. TOOGOOD, J. Chem. Soc. *1949*, 1890. – E. A. BRAUDE and E. R. H. JONES, J. Amer. Chem. Soc. *72*, 1041 (1950).

it may involve greater steric hindrance to planarity than the *s-cis*, is borne out by the X-ray diffraction work of MACGILLAVRY and her collaborators on β-ionylidenecrotonic acid[1]. Another effect shown by the dienones is the emergence of a band due to a partial (enone) chromophore; as the interaction between the ring-double bond and the side-chain becomes sterically more and more inhibited, the probability of the independent transition of the enone group giving rise to a band near 2300 Å, progressively increases[2].

Table VIII.–Steric Effects in Substituted Butadienes

	$\lambda_{max.}$, Å	ε	$\varepsilon/\varepsilon_0$	Θ_1^0
$CH_2{=}CH\text{-}CH{=}CH_2$ . .	2,170	21,000	1·0	0
$MeCH{=}CH\text{-}CH{=}CH_2$.	2,230	23,000	1·0	0
$MeCH{=}CH\text{–}CH{=}CHMe$	2,270	24,000	1·0	0
$Me_2C{=}CH\text{–}CMe{=}CH_2$.	2,320	8,500	0·35	53
$Me_2C{=}CH\text{–}CCl{=}CH_2$ . .	2,330	8,100	0·34	55
$Me_2C{=}CH\text{–}CH{=}CMe_2$.	2,410	24,000	1·0	0
$Cl_2C{=}CCl\text{–}CCl{=}CCl_2$ . .	<2,100	—	<0·1	>70

Acyclic and Homocyclic dienes. The stereochemistry of the central bond in butadiene was first explicitly considered in 1939 by MULLIKEN[3], who deduced a planar *s-trans* conformation on theoretical grounds. This was later confirmed experimentally by ASTON and coworkers[4] by thermodynamic measurements, and is also in agreement with electron diffraction[5] and Raman spectroscopic[6] studies. Similar conclusions have been reached for butadienes containing either one or two methyl or chloro-substituents[7]; scale-diagrams indicate that, independently of the positions of two substituents (e.g. 1:1-, 1:2-, 2:3-, or 1:4-) the planar *s-trans* conformations of such dienes are unhindered, and the ultraviolet spectra are "normal" (table VIII). Uniplanarity is also unopposed by three or even four substituents in the terminal (1:4) positions, but not in 1:1:3-trisubstituted butadienes (Fig. 13); the latter exhibit marked by lower ε values from which can be calculated interplanar angles of *ca.* 50°. In penta- and hexa-substituted butadienes, hindrance is so large that the K-bands disappear altogether[7].

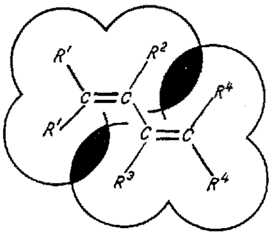

Fig. 13.–Planar projection of substituted butadienes.

Table IX.
Ultraviolet Spectra and Conformations of 1:3-Cycloalkadienes[1]

Ring size	$\lambda_{max.}$, Å	ε	Favoured Conformation[a]	Θ_1[a]	Θ_1[b]
C_5	2,385	3,400	Near-planar *cis-s-cis-cis*	~ 0°	–
C_6	2,560	8,000	Near-planar *cis-s-cis-cis*	~ 0°	–
C_7	2,480	7,400	Near-planar *cis-s-cis-cis*	~ 0°	–
C_8	2,280	5,600	Non-planar *cis-s-cis-cis*	~45°	41°
C_9	2,195	2,500	Non-planar *cis-s-cis-trans*	~60°	60°
C_{10}	2,230	5,000	Non-planar *cis-s-trans-trans*	~60°	60°
C_{11}	2,250	6,200	Non-planar *cis-s-trans-trans*	~60°	56°

[a] Deduced from models. [b] Calculated from ε.

In homocyclic dienes, the conformation of the conjugated system is closely dependent on the ring size[1]. In the small rings (C_5–C_7), the diene systems must all be approximately planar and *cis-s-cis-cis* oriented. The differences in spectral properties relative to acyclic dienes observed in these cases (table IX) appear to be primarily electronic in origin and to be associated with hyperconjugation involving the saturated carbon atoms, and with transannular conjugation of the double bonds.

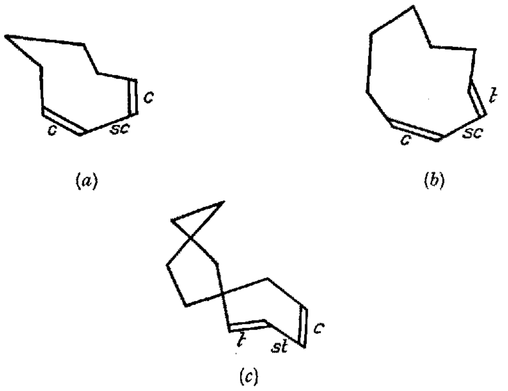

Fig. 14.–Conformations of (*a*) *cyclo*octa-1:3-diene, (*b*) *cyclo*nona-1:3-diene, and (*c*) *cyclo*deca-1:3-diene.

In the medium-size rings (C_8–C_{12}), models indicate that the diene system will be non-planar and that the conformations shown in Figure 14 will be favoured; the angles deduced from the spectral data are in excellent agreement. The small, but significant differences in $\lambda_{max.}$ indicate that although the excited states are near-planar, the steric effects are large enough to affect the energy levels by up to about 5 kcal/mol.

Zusammenfassung

Die Faktoren, welche die labile Stereochemie von konjugierten Systemen beeinflussen, werden diskutiert. Das Studium der Elektronenspektren solcher Systeme zeigt, dass in vielen Fällen Moleküle, welche in vorwiegend unebenen (nichtplanaren) Grundzuständen existieren, in vorwiegend ebene (planare) erregte Zustände übergehen. Die Gleichgewichtskonstellationen werden abgeleitet für Biphenylderivate, Arylketone, Styrole, Arylamine, Cyclohexenderivate und cyclische und acyclische Diene.

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[1] C. H. MACGILLAVRY, A. KREUGER, and E. L. EICHHORN, Proc. Acad. Sci. Amst. *B 54*, 449 (1951), and private communication from Professor MACGILLAVRY.

[2] E. A. BRAUDE *et al.*, loc. cit.

[3] R. S. MULLIKEN, J. Chem. Physics *7*, 121 (1939).

[4] J. G. ASTON, G. SZASZ, H. W. WOOLEY, and F. G. BRICKWEDDE, J. Chem. Physics *14*, 67 (1946).

[5] V. SCHOMAKER and L. PAULING, J. Amer. Chem. Soc. *61*, 1769 (1939).

[6] K. BRADACS and L. KAHOVEC, Z. physikal. Chem. *B 48*, 635 (1940).

[7] G. J. SZASZ and N. SHEPPARD, Trans. Faraday Soc. *49*, 358 (1953).

[1] E. A. BRAUDE, Chem. and Industry *1954*, 1557. – In a recent paper, A. T. BLOMQUIST and A. GOLDSTEIN [J. Amer. Chem. Soc. *77*, 998 (1955)] have described the *cis-cis*-isomer of *cyclo*deca-1:3-diene which shows *no* band in the 2150–2300 Å region, indicating that the diene system in this isomer is highly non-planar.