Infrared Intensities as a Measure of Intramolecular Interactions. Part XXXVI.[1] Field-induced Resonance Effects

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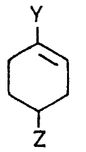
The variation of the $\nu_{C=O}$ intensity for a series of disubstituted cyclohexenes indicates that the resonance interaction of a substituent with the unsaturated system can be altered by a second remote substituent. This effect is ascribed to the operation of a field-induced resonance effect.

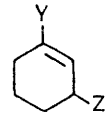
THE electric effects of substituents have attracted much interest over recent years and various possible modes of interaction have been suggested.[2,3] In the absence of π-systems, electric disturbances caused by a substituent arise from the C–Y dipole or any charge on Y (inductive effects). These disturbances can be felt elsewhere by a through space electrostatic mechanism (field effect) and this has been demonstrated [4] to be of considerably more significance than transmission by progressive relay of induced charge (σ-inductive effect) through the carbon chains of molecules once past the attached carbon atom. When a substituent is attached to a π-system then resonance or hyperconjugative interactions can occur in which electronic charge is transferred between the substituent and the π-system. It has also been suggested that the inductive effect of the C–Y group can polarise the π-system (π-inductive effect) although this is a matter of dispute.[2,5] Certain other non-bonded electrostatic interactions and secondary effects have also been suggested.[2]

When two substituents are attached to a π-system, such as in a disubstituted benzene, additional resonance interactions can occur depending on the electrical effect of each substituent on the other. The most discussed of these is the ' through-conjugation ' that can occur when a resonance-donating substituent can conjugate with a resonance-accepting substituent such as in *para*-nitroaniline and a considerable amount of evidence is available in support. Suggestions that the π-inductive effect of one substituent may lead to a change in the π-system of the benzene ring and then to a change in the resonance interaction between the second substituent and the ring have also been advanced.[6] Some of our recent results [7,8] have suggested that changes in the resonance interaction between the ring and a substituent follow the overall effect (inductive + resonance) of the other substituent. This indicates that the polar (inductive) nature of one substituent might affect the resonance interaction of the other but we are not in support of the mechanism *via* an intermediate π-inductive effect above since we believe [2] this latter effect to be small.

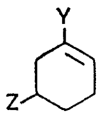
The question thus arises as to whether a remote substituent can affect the resonance interaction of a second substituent joined to a π-system *via* a through space electrostatic (field) mechanism. Clearly it is not easy to directly distinguish such affects in disubstituted benzenes because of the multiplicity of modes of electron disturbance that exist. We therefore have synthesised a series of further substituted 1-methoxy- and 1-chlorocyclohexenes to establish if the remote substituent leads to changes in the resonance interaction between the double bond and the methoxy- or chloro-group (Y). Evidence [8-10] from resonance interactions in α-substituted toluenes or β-substituted ethylbenzenes shows that such substitution has little effect compared with the parent compound. The systems above also allow for a controlled geometry although equatorial or axial conformations are possible for C–Z with respect to C–Y. This has been investigated for certain disubstituted cyclohexenes (see below) but does not effect the general conclusions drawn in the present investigation.



(I)
Z=H,Me,CN



(II)
Z=H,Me,Br,CN



(III)
Z=H,CN

The intensity of the $\nu_{C=O}$ stretching mode has been shown [11] to be a measure of the resonance interaction between a substituent and the π-system of substituted ethylenes and this was the method adopted to study similar interactions in the cyclohexenes. The form of the vibration does not change greatly in simple substituted ethylenes [11] and this is substantiated by the relative constancy of the frequency in each series reported here.

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EXPERIMENTAL

The compounds were characterised by a combination of physical constants, i.r. and n.m.r. spectroscopy, and elemental analysis. Their purity was confirmed by g.l.c. The n.m.r. spectra were recorded on a Varian T60 spectrometer using carbon tetrachloride as a solvent. Quantitative i.r. spectra were recorded on a Perkin-Elmer model 225 spectrophotometer using a 0·01 cm potassium bromide cell and carbon tetrachloride solvent. The detailed procedure and the method of determining the intensities by a modification[12] of the 'Bandfit' program of Fraser and Suzuki[13] have been described elsewhere.[12] The program utilises additional peaks to ensure accurate band-fitting where the spectral traces are not symmetrical but this does not necessarily imply that there are other absorptions present. Some small peaks occurring at distances greater than the band halfwidth have been omitted but their inclusion throughout does not alter the conclusions reached.

References to the literature methods used to prepare most of the compounds together with the spectral data are given in Table 1. The other samples were prepared as below.

TABLE 1

Physical and spectral properties of substituted cyclohexenes

Substituents		Ref. to prepar-	$\nu_{C=C}$/cm^{-1}		A/
1-	Other	ation	*a*	*b*	l mol^{-1} cm^{-2} [c]
H	H	*e*	1652	1652	125
	3-CN	Text	1653	1654	139
	4-CN	*f*	1653	1653	142
	4-Me	*g*	1651	1651	178
	3-Br	*h*	1641	1654, 1641	220
Cl	H	*i*	1657	1657, 1648	632
	3-CN/ 5-CN [d]	Text	1656	1661, 1656, 1626	883
	4-CN	*f*	1660	1660, 1640	877
	4-Me	*j*	1657	1657	510
	3-Br	*k*	1641	1662, 1649, 1641, 1631	1661
OMe	H	20	1667	1667	2843
	3-CN/ 5-CN [d]	Text	1666	1673, 1666	3405
	4-CN	Text	1670	1670	3592
	4-Me	Text	1666	1673, 1667	2851
	6-Br	Text	1657	1658, 1657	2304

[a] Measured peak maxima. [b] Values used in peak fitting program (see text). [c] Solutions in carbon tetrachloride. [d] *ca.* 40% of 3-isomer (see text). [e] A. Vogel, 'A Textbook of Practical Organic Chemistry,' Longmans, London, 1957, 3rd edn., p. 243. [f] A. A. Petrov and N. P. Sopov, *J. Gen. Chem. U.S.S.R.*, 1947, **17**, 2228. [g] Purified from commercial sample. [h] A. T. Blomquist and T. Kwiatek, *J. Amer. Chem. Soc.*, 1951, **73**, 2098. [i] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1950, 2014. [j] N. A. Domnim, *J. Gen. Chem. U.S.S.R.*, 1939, **9**, 1983. [k] N. Mousseron, F. Winternitz, and R. Jacquier, *Compt. rend.*, 1947, **224**, 1062.

3-*Cyanocyclohexene*.—This was prepared by treating 3-bromocyclohexene (10 g) with dried, freshly prepared cuprous cyanide (6·5 g) and a trace of potassium iodide in an anhydrous atmosphere at 55° for 8 h. The reaction mixture was treated with saturated potassium cyanide, extracted with chloroform, dried, concentrated, and fractionated to yield 3-cyanocyclohexene (2·3 g), b.p. 83—85° at 15 mmHg (lit.,[14] 88—89° at 17 mmHg), $\nu_{max.}$ 2252 and 1654 cm^{-1} (Found: C, 78·25; H, 8·4; N, 13·05. Calc. for C_7H_9N: C, 78·5; H, 8·4; N, 13·1%).

3- *and* 5-*Cyano*-1-*chlorocyclohexenes*.—3-Cyanocyclohexanone was prepared from cyclohex-2-enone[15] by the addition of hydrogen cyanide in glacial acetic acid–ethanol as described by Banerjee *et al.*[16] 3-Cyanocyclohexanone reacted with phosphorus pentachloride to give a mixture of 3- and 5-cyano-1-chlorocyclohex-1-enes. To phosphorus pentachloride (12 g) in dry ether (20 ml) was added 3-cyanocyclohexanone (7 g) at 25°. The mixture was stirred for 8 h, washed (dilute hydrogen carbonate solution), dried ($MgSO_4$), and concentrated. The crude 1-chlorocyanocyclohexene (6·3 g) was heated with pyridine (1·0 g) to eliminate HCl from some 1,1-dichloro-3-cyanocyclohexane also present and distilled at 126—127° and 25 mmHg. G.l.c. analysis showed two compounds were present in the ratio *ca.* 1 : 2, $\nu_{max.}$ 2248 and 1657 cm^{-1} (Found: C, 59·8; H, 5·75; N, 9·7. Calc. for C_7H_8ClN: C, 59·55; H, 5·65; N, 9·95%). The isomers were identified by g.l.c.–mass spectrometry.

The predominant isomer (61%) had a strong $P - 53$ peak in its mass spectrum in accord with that found for 4-cyanocyclohexene while the other isomer had a strong $P - 28$ peak in accord with that found for 3-cyanocyclohexene. The predominant isomer is therefore taken to be 1-chloro-5-cyanocyclohexene. The compounds could not be separated by chromatography but use of silica gel with benzene–light petroleum (7 : 3) as eluant allowed the isolation of a mixture containing 67% of 1-chloro-5-cyanocyclohexene and 33% of 1-chloro-3-cyanocyclohexene. I.r. intensity measurements on the two isomer mixtures allowed approximate intensities to be ascribed to each isomer.

3- *and* 5-*Cyano*-1-*methoxycyclohexenes*.—3-Cyanocyclohexanone reacted with trimethyl orthoformate to give a mixture of 3- and 5-cyano-1-methoxycyclohexenes. Trimethyl orthoformate (2·6 g) was added to a solution of mesitylenesulphonic acid (0·02 g) and 3-cyanocyclohexanone (2·5 g) in dry methanol (5 ml). After refluxing for 8 h, mesitylenesulphonic acid (0·01 g) was added and the mixture distilled. The product was collected at 118—119° and 17 mmHg, $\nu_{max.}$ 2850, 2245, and 1670 cm^{-1}, δ 4·62 (1H, m), 3·52 and 3·48 (3H, d), 3·4 and 2·9 (1H, m), and 2·1 (6H, m) (Found: C, 70·2; H, 8·15; N, 10·1. Calc. for $C_8H_{11}NO$: C, 70·0; H, 8·1; N, 10·2%). Comparison of the n.m.r. spectrum with that of 3- and 4-cyanocyclohexenes and with that of 1-methoxycyclohexene indicated that the peak at δ 3·4 arose from 3-H in the 3-cyano-compound and that at δ 2·9 from 5-H in the 5-cyano-compound. Integration gave the composition as *ca.* 65% of 5-cyano-1-methoxycyclohexene.

4-*Cyano*-1-*methoxycyclohexene*.—2-Methoxybutadiene[17,18] (2·58 g), acrylonitrile (2·0 g), toluene (8 ml), and a trace of pyrogallol were heated for 12 h at 145° in a sealed tube. The mixture was fractionated and the product (1·8 g) obtained, b.p. 132—136° at 30 mmHg (lit.,[19] 125—126° at

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20 mmHg), $\nu_{max.}$ 2868, 2251, and 1670 cm^{-1}, δ 2·15 (6H, m), 2·72 (1H, q), 3·53 (3H, s), and 4·57 (1H, t).

1-*Methoxy*-4-*methylcyclohexene*.—Trimethyl orthoformate (26 g) was added [20] to 4-methylcyclohexanone (20 g), methanol (40 ml), and mesitylenesulphonic acid (0·2 g). The mixture was refluxed for 16 h, mesitylenesulphonic acid (0·1 g) added, and the product obtained by distillation, b.p. 160—161° at 760 mmHg. Unchanged starting material was removed by elution of the product from alumina with light petroleum (b.p. 40—60°), $\nu_{max.}$ 1657 cm^{-1}, δ 1·0 (3H), 2·0 (7H), 3·6 (3H), and 4·8 (1H).

6-*Bromo*-1-*methoxycyclohexene*.[15] This was purified by elution from alumina with light petroleum (b.p. 40—60°) and distilled at 54—56° and 1 mmHg (lit.,[15] 49° at 0·2 mmHg), $\nu_{max.}$ 1656 cm^{-1} (C=C), δ 2·2 (6H), 3·75 (3H), 4·7 (1H), and 4·9 (1H).

RESULTS AND DISCUSSION

Geometry of the Cyclohexene Derivatives.—As indicated in the Introduction the actual geometry does not affect our qualitative observations but would need to be established in order to reach quantitative conclusions. The three-dimensional structure of cyano-substituted 1-chlorocyclohexenes has been discussed [21a] on the basis of the results of dipole measurement studies. It was expected [21b] from previous work on the bromocyclohexenes that when a substituent is introduced into a six-membered ring then the axial form becomes preferred for a 4-substituent. However, it was concluded [21b] that the cyano-group occupied predominantly (79%) the equatorial portion in 4-cyano-1-chlorocyclohexene. The equatorial position was also favoured (64%) by the cyano-group in 3-cyanocyclohexene.[21a] The small differences in free energy between the axial and equatorial forms and the variation observed suggest that detailed studies would be necessary to establish the conformation equilibrium in each case of interest. Models indicate that the electrical effect of the dipole of a 3- or 4-substituent will be greater along the axis of a substituent–carbon bond from an equatorial arrangement than from an axial one. The results below must therefore not be used in a quantitative sense.

The methoxy-group can also assume either a planar *cis*- or *trans*-configuration relative to the double bond in 1-methoxycyclohexenes. It has been shown [22] that the *cis*-configuration is preferred in substituted ethylenes and models show that the effect of neighbouring hydrogen atoms will reinforce this preference in the cyclohexene.

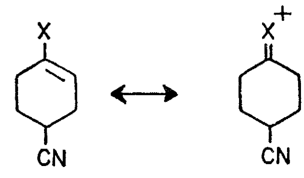
Field-induced Resonance.—Previous work [11] has shown that resonance interactions in substituted ethylenes are proportional to the $A^{\frac{1}{2}}$ values for the $\nu_{C=C}$ absorptions. For convenience we therefore list our results in this form in Table 2. The intensity of the $\nu_{C=C}$ vibration in cyclohexene itself is low as expected for a *cis*-1,2-dialkyl-substituted alkene. The value is not significantly changed by the introduction of a 3- or 4-cyano-group.

TABLE 2

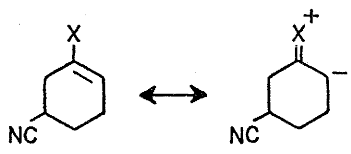
$A^{\frac{1}{2}}$ Values for disubstituted cyclohexenes

	$A^{\frac{1}{2}}$/l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ cm^{-1}					
x-Substituent	H	3-CN	4-CN	4-Me	3-Br	6-Br
1-Substituent						
H	11·2	11·8	11·9	13·3	14·8	
Cl	25·1	(39·5)	29·6	22·6	40·8	
OMe	53·3	>58·4	59·9	53·4		48·0

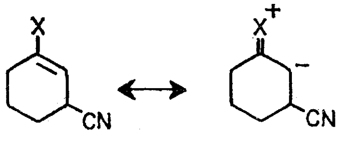
The intensity of 1-chlorocyclohexene is considerably greater than the unsubstituted compound and that for the 1-methoxy-compound is greater again as expected in terms of their resonance interactions. The introduction of a 4-methyl substituent makes little difference to the intensity of the 1-methoxy-compound and causes a decrease in the 1-chlorocyclohexene. The introduction of a 4-cyano-group by contrast leads to a significant increase in intensity in both cases. These results are only apparently explicable in terms of a field-induced resonance effect. The strong dipole of the cyano-group leads to an increased resonance interaction between the chloro- or methoxy-group and the double bond. In valence-bond terminology the cyanide group lowers the energy of the canonical form (V) by a charge–dipole interaction. The methyl group would be expected to have only a weak effect in the opposite direction in accord with the results.



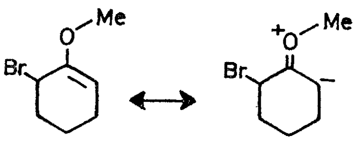
(IV) (V)



(VI) (VII)



(VIII) (IX)



(X) (XI)

We attempted to synthesise the corresponding

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3-cyano-compounds. Unfortunately in both cases we obtained mixtures of the 3- and 5-cyano-isomers which could not be completely separated. The proportion and identity of each was established by g.l.c., mass spectral, and n.m.r. examination of mixtures obtained with varying percentages of the two forms. I.r. intensity measurements on such mixtures indicated that the introduction of a 5-cyano-substituent led to a decrease in intensity of the parent chlorocyclohexene compound, while the 3-cyano-substituent caused an increase. The lack of increase in the former case is probably understandable in terms of the geometry of the group relative to the double bond. In form (VII) the cyano-dipole is similarly placed relative to both the positive and negative charges of the canonical form and its energy will not be lowered compared to the corresponding structure of cyclohexene itself.

The significant increase in intensity (Table 1) found in the mixtures of 3- and 5-cyano-1-chlorocyclohexenes and 1-methoxycyclohexenes compared with the parent compounds thus stems primarily from the 3-cyano-isomers. Clearly the 3-cyano-group causes a bigger increase in resonance interaction from the chloro- or methoxy-group than one in the 4-position. This probably reflects mainly the closer position of the dipole to the charge separation with some help to canonical form (IX) caused by a σ-inductive effect being possible.

The 3-bromo-substituent likewise leads to a great increase in intensity in 3-bromo-1-chlorocyclohexene. By contrast introducing a 6-bromo-substituent into 1-methoxycyclohexene led to a large decrease in intensity. This apparent decrease in methoxy–π interaction is explicable in terms of a field affected resonance interaction since models indicate that the C–Br dipole will have more affect on the positive end (destabilising) of the methoxy–double bond dipole, *i.e.* form (XI) will be of higher energy than in the absence of the bromine substituent.

Our results can thus only be readily explained by the presence of field-induced resonance effects which will clearly depend on the polarisability of the substituent in the 1-position, on the dipole of the second substituent and on their relative geometry. We hope to provide further evidence for such effects in substituted benzenes in future work.

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