The Infrared Spectra of Some Esters, Nitriles, and Ester-nitriles.

By D. G. I. FELTON and S. F. D. ORR.

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The unsaturated compound diethyl 1 : 2-dicyanoethylene-1 : 2-dicarboxylate was found to give a C:O band in a position close to that expected for a saturated ester but a C⋮N band in that expected for an unsaturated ester, and a very weak C:C band was also found. This behaviour has been explained on the basis of the electronic structure of the molecule by taking into account the appropriate inductive, mesomeric, and steric factors. Such an explanation has been made possible by a careful examination of these factors as they affect the C:O, C⋮N, and C:C frequencies in simple esters and nitriles and in related ester-nitriles.

IT has been shown (Felton, *J.*, 1955, 515) that oxidation of ethyl cyanoacetate by selenium dioxide yields diethyl 1 : 2-dicyanoethylene-1 : 2-dicarboxylate. Before this structure had been proved, the infrared spectrum of the compound was examined in order to decide between the two alternative structures then thought possible, *viz.*, the above and triethyl 1 : 2 : 3-tricyano*cyclo*propane-1 : 2 : 3-tricarboxylate. It was expected that these would readily be differentiated by comparison of the frequency of the ester-carbonyl band with that in the parent ethyl cyanoacetate, as a reduction of some 20 cm.$^{-1}$, due to the conjugation with the double bond, would be expected only for the former structure. This structure would also be expected to have a lower nitrile frequency and to exhibit an ethylene stretching frequency at about 1600 cm.$^{-1}$.

The oxidation product was found to give a carbonyl band at a position only slightly lower than in ethyl cyanoacetate, *viz.*, at 1750 cm.$^{-1}$ compared with 1754 cm.$^{-1}$ (both in carbon tetrachloride solution). The nitrile band, however, was lowered from 2267 to 2229 cm.$^{-1}$ and a weak band at 1600 cm.$^{-1}$ was found (all in chloroform solution). Later, it was shown unequivocally that the oxidation product possessed the olefinic structure. The question then arose as to why the carbonyl frequency is higher than expected.

A series of related ester-nitriles and a number of simple esters and nitriles have been examined and the bands due to their carbonyl, nitrile, and olefinic groups, where present, have been measured in dilute solutions in carbon tetrachloride and chloroform. The values found are shown in the Tables. Previous measurements, to which reference is made in the

TABLE 1. *Frequencies* (ν *in cm.*$^{-1}$) *and intensities* (ε *in l. mole*$^{-1}$ *cm.*$^{-1}$) *for bands due to carbonyl and olefinic groups in esters.*

	C:O band frequencies:		C:C band in $CHCl_3$	
	in CCl_4	in $CHCl_3$	ν	ε
1. Ethyl acetate	1744	1733	—	—
2. Ethyl propionate	1740	1728	—	—
3. Diethyl malonate	1740 1757	1731 1747	—	—
4. Diethyl succinate	1740	1732	—	—
5. Tetraethyl ethanetetracarboxylate	1742 1751	1737 1746	—	—
6. Ethyl crotonate	1724	1712	1662	120
7. Ethyl α-methylacrylate	1721	1712	1638	81
8. Ethyl 3-methylbut-2-enoate	1720	1705	1654	170
9. Diethyl *iso*propylidenemalonate	1726	1719	1640	115
10. Diethyl fumarate	1727	1719	1647	95
11. Diethyl maleate	1734	1724	1646	95
12. Diethyl mesaconate	1725	1716	1649	110
13. Diethyl citraconate	1732	1723	1653	160
14. Tetraethyl ethylenetetracarboxylate	1739 1750	1737 1750	1651	35

TABLE 2. *Frequencies and intensities for the bands due to nitrile and olefinic groups in nitriles.* (ν_{weak} refers to the frequencies of bands accompanying the main C⋮N band with less than 10% of its intensity. ν_{Ar} and ε_{Ar} refer to bands arising from the presence of an aromatic structure.)

	C⋮N bands in $CHCl_3$			C:C bands in $CHCl_3$			
	ν	ε	ν_{weak}	ν	ε	ν_{Ar}	ε_{Ar}
15. Acetonitrile	2292 2255	13 32	—	—	—	—	—
16. Butyronitrile	2253	34	2293	—	—	—	—
17. Malonodinitrile	2273	7	2292	—	—	—	—
18. Succinodinitrile	2256	27	2275	—	—	—	—
19. Acrylonitrile	2231	38	2277	1647 1610	2·7 3·4	—	—
20. Crotononitrile	2228	81	—	1638	38	—	—
21. α-Methylacrylonitrile	2229	42	2210	1626	18	—	—
22. 3-Methylbut-2-enonitrile	2221	150	—	1637	32	—	—
23. (1-Ethylpropylidene)malonodinitrile	2234	110	—	1591	100	—	—
24. Benzylidenemalonodinitrile	2232	140	—	1594	180	1572	120
25. 1-Phenylethylidenemalonodinitrile	2230	93	—	1587	92	1568	100
26. Fumarodinitrile	2240	14	2260 2229	1612	3	—	—
27. Maleidinitrile	2251 2231	5·8 5·4	—	1630 1599	1·3 1·8	—	—
28. Mesaconodinitrile	2236	34	2226	1637 1616	10 11	—	—
29. Dimethylfumarodinitrile	2231	70	—	1645 1615	7 15	—	—
30. Dimethylmaleidinitrile	2224	51	—	1614	11	—	—
31. 3 : 4 : 5 : 6-Tetrahydro-*o*-phthalodinitrile	2227	61	—	1616	9	—	—
32. Phenylfumarodinitrile	2234 2223	20 24	—	1592	39	1570	42
33. Phenylmaleidinitrile	2225	62	2234	1590	51	1574	59
34. Methylphenylfumarodinitrile	2229	57	2219	1597	8	1576	9
35. Methylphenylmaleidinitrile	2226	57	—	1593	10	1577	10
36. Diphenylfumarodinitrile	2224	62	—	1619	10	1582	10

TABLE 3. *Frequencies and intensities for the bands due to carbonyl, nitrile, and olefinic groups in ester-nitriles.*

	C:O band frequencies:		C⋮N band in $CHCl_3$		C:C band in $CHCl_3$	
	in CCl_4	in $CHCl_3$	ν	ε	ν	ε
37. Ethyl cyanoacetate	1754	1751	2267	14	—	—
38. Diethyl 1 : 2-dicyanoethane-1 : 2-dicarboxylate	1755	1754	2259	13	—	—
39. Triethyl 1 : 2 : 3-tricyano*cyclo*propane-1 : 2 : 3-tricarboxylate	1765	1765	2260	10	—	—
40. Ethyl 2-cyanopent-2-enoate ...	1737	1732	2233	43	1602	132
41. Ethyl 2-cyano-3-ethylpent-2-enoate	1732	1727	2224	65	1629	123
42. Ethyl *trans*-*β*-cyanocrotonate	1728	1723	2228	28	1637	92
43. Ethyl *cis*-*β*-cyanocrotonate ...	1738 1725 (sh)	1728	2229	17	1642	80
44. Diethyl *trans*(?)-1 : 2-dicyanoethylene-1 : 2-dicarboxylate	1750	1747	2229	10	1600	6

Discussion, have been made on the simpler compounds, but these have not always been on dilute solutions. Only under the latter conditions can spectral changes due to causes other than structure be eliminated, so all values used have been determined in this work.

EXPERIMENTAL

Materials.—Ethyl acetate and propionate, diethyl malonate and succinate, ethyl α-methylacrylate and cyanoacetate and aceto- and butyro-nitrile, malono- and succino-dinitrile, and acrylo- and α-methylacrylo-nitrile were commercial samples, redistilled when required. Tetraethyl ethanetetracarboxylate, m. p. 76·5—77·5° (corr.), was prepared according to Mann and Saunders (" Practical Organic Chemistry," Longmans Green and Co., London, 1938, p. 190), and tetraethyl ethylenetetracarboxylate, m. p. 55·5—56·5° (corr.), according to Corson and Benson (*Org. Synth.*, Coll. Vol. II, p. 273). Diethyl *iso*propylidenemalonate, b. p. 118—120°/16 mm., n_D^{23} 1·4475, was prepared by Cope and Hancock's method (*J. Amer. Chem. Soc.*, 1938, **60**, 2645). Ethyl 3-dimethylbut-2-enoate, b. p. 60°/20 mm., n_D^{20} 1·4368, diethyl fumarate, b. p. 114—116°/15 mm., and diethyl maleate, b. p. 110—112°/16 mm., were obtained from the corresponding acids by azeotropic esterification, and diethyl citraconate, b. p. 114°/12 mm., $n_D^{20\cdot5}$ 1·4439, and diethyl mesaconate, b. p. 110°/16 mm., $n_D^{19\cdot5}$ 1·4484, were prepared according to Jeffery and Vogel (*J.*, 1948, 658).

3-Methylbut-2-enonitrile, b. p. 138—142°, $n_D^{21\cdot5}$ 1·4320, was prepared by distilling *iso*butyraldehyde cyanohydrin (Ultée, *Rec. Trav. chim.*, 1909, **28**, 7) over phosphoric oxide at atmospheric pressure (De Laet, *Bull. Soc. chim. belg.*, 1929, **38**, 163). (1-Ethylpropylidene)malonodinitrile, b. p. 114—115°/15 mm., n_D^{26} 1·4689, was prepared according to Cope and Hoyle (*J. Amer. Chem. Soc.*, 1941, **63**, 733), benzylidenemalonodinitrile, m. p. 86° (corr.), according to Corson and Stoughton (*ibid.*, 1928, **50**, 2825), and 1-phenylethylidenemalonodinitrile, m. p. 92·5—93·5° (corr.), according to Mowry (*ibid.*, 1943, **65**, 991). Fumarodinitrile, m. p. 97·5—98·5° (corr.), was obtained following the procedure of Mowry and Butler (*Org. Synth.*, 1950, **30**, 46), and maleidinitrile, m. p. 30—31° (corr.), following that of Linstead and Whalley (*J.*, 1952, 4839).

Ethyl 2-cyanopent-2-enoate, b. p. 115—120° (bath)/16 mm., was prepared by esterification of the acid (von Auwers, *Ber.*, 1923, **56**, 1172), and ethyl 2-cyano-3-ethylpent-2-enoate by Cope and Hancock's procedure (*Org. Synth.*, 1945, **25**, 46). Ethyl *cis*- (b. p. 116—118°/20 mm., n_D^{21} 1·4530) and *trans*-β-cyanocrotonate (b. p. 93—95°/20 mm., n_D^{21} 1·4508) were prepared according to Mowry and Rossow (*J. Amer. Chem. Soc.*, 1945, **67**, 926). The infrared spectrum of the *cis*-isomer gave an unexpected shoulder on the low-frequency side of the ester-carbonyl band, but this was not due to contamination with the *trans*-isomer. Through the courtesy of Dr. Mowry (Monsanto Chemical Co., St. Louis, Mo., U.S.A.) the original sample of the *cis*-isomer was obtained and its infrared spectrum was identical in all respects with that of the above sample.

The preparation of diethyl *trans*(?)-1 : 2-dicyanoethylene-1 : 2-dicarboxylate and of triethyl 1 : 2 : 3-tricyano*cyclo*propane-1 : 2 : 3-tricarboxylate has already been described (Felton, *J.*, 1955, 515 *).

Diethyl αβ-Dicyanosuccinate.—Diethyl 1 : 2-dicyanoethylene-1 : 2-dicarboxylate (2·2 g.) in ethanol (200 ml.) was shaken at room pressure and temperature with hydrogen and Adams's platinic oxide catalyst. After the uptake of 1 mol. of hydrogen, the catalyst was removed, the

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* On line 20 of *J.*, 1955, 516, the temperature should read 120°.

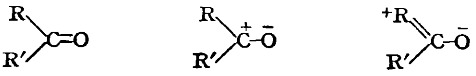
solvent evaporated, and the residue distilled to yield the *succinate*, b. p. 190—200° (bath)/10 mm. (Found : C, 53·9; H, 5·15; N, 12·8. $C_{10}H_{12}O_4N_2$ requires C, 53·6; H, 5·4; N, 12·5%).

Samples of crotononitrile, mesacono-, dimethylfumaro-, phenyl-malei- and -fumaro-, and methylphenyl-malei- and -fumaro-dinitrile (Beech and Piggott, *J.*, 1955, 423) and diphenylfumarodinitrile (Timmons and Wallwork, *Chem. and Ind.*, 1955, 62) were obtained from Imperial Chemical Industries Limited, Dyestuffs Division, through the great courtesy of Dr. M. A. T. Rogers; Drs. J. A. Elvidge and M. Whalley (Imperial College of Science and Technology, London, S.W.7) kindly provided samples of dimethylmaleidinitrile and 3 : 4 : 5 : 6-tetrahydro-*o*-phthalodinitrile.

Infrared Spectra.—The spectra were measured on a Perkin-Elmer Model 112 spectrometer. A rock-salt prism was used for the measurement of the carbonyl and olefinic bands (6μ) and one of lithium fluoride for the nitrile bands (4·5μ). The instrument was kept at a carefully controlled temperature, and the calibration checked repeatedly; as a result, the error in frequency in both regions cannot be more than ±2 cm.$^{-1}$, and duplicate measurements all agreed to within 1 cm.$^{-1}$. Solutions were measured in a 1 mm. cell and the intensities are quoted as approximate extinction coefficients (± about 10%) at the band maximum in l. mole^{-1} cm.$^{-1}$.

DISCUSSION

It is well known that the frequency of a band due to the stretching of a multiple bond is dependent on the electronic structure around this bond, and in particular on its bond order. Thus, for carbonyl compounds the frequency due to this group has been considered (Hartwell, Richards, and Thompson, *J.*, 1948, 1436) in relation to the actual resonance



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

hybrid made up of the three forms (*a*)—(*c*). The relative importance of these forms will depend on the nature of the group R (and R′), and this may be considered in relation to the electronic shifts it produces by reason of its inductive or mesomeric effect. In addition, it is necessary, when conjugation between two unsaturated groups can occur, to take into account possible steric factors. If the necessary spatial arrangements do not allow a coplanar structure for two multiple bonds on either side of a single bond, the two π-orbitals will no longer be able to overlap to the fullest extent and conjugation will be either reduced or eliminated entirely. Conjugation can also be affected by changes in bond angles induced by steric repulsion between two similarly charged polar groups in close proximity, but then an increase or a decrease in conjugation can occur.

Previous applications of such considerations have been made mainly in cases where a single effect is operative and do not cover many of the frequency values now reported, especially those of the polyfunctional compounds. Two main effects have been discussed in the case of esters : first, the inductive effect of an electrophilic group on the α-carbon atom, which reduces the contributions to the resonance hybrid of the ionic forms (*b*) and (*c*) and thus increases the C:O frequency, has been observed for α-halogeno- and α-cyano-acetates (Hartwell, Richards, and Thompson, *loc. cit.*; Hampton and Newell, *Analyt. Chem.*, 1949, **21**, 914; Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073); and, secondly, the mesomeric effect of an unsaturated group leads to increased contributions of the ionic forms owing to their stabilisation by the greater separation of charge, and the consequent reduction in C:O frequency has been observed in both olefinic and aromatic esters (Hartwell, Richards, and Thompson; Hampton and Newell; Ramussen and Brattain, *locc. cit.*). In the case of the nitriles, the C:N bands of a large number, including compounds 15—21, 26, and 29 in the Tables, have been measured by Kitson and Griffith (*Analyt. Chem.*, 1952, **24**, 334) and the reduction in frequency consequent on conjugation with an unsaturated centre has been pointed out.

These explanations have been made to cover the larger shifts in the positions of the C:O and C:N bands, but there is no doubt that even small shifts, when obtained for solutions in the same solvent, are significant and can be correlated with structure on the same basis, as has been shown for keto-steroids and steroid esters (Jones, Humphries, and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 956). Thus, the slight reduction of C:O frequency in ethyl propionate (2) compared with ethyl acetate (1) is in line with the greater electron-repelling effect of methyl than of hydrogen; the strongly electron-attracting nitrile group produces a shift, which is both larger and in the opposite direction, of 10 cm.$^{-1}$ between ethyl acetate (1) and ethyl cyanoacetate (37). A similar increase would be expected with diethyl malonate (3), but splitting of the C:O band precludes its observation, although the mean position of the two components is certainly above that of the band in ethyl acetate. A similar situation arises in tetraethyl ethanetetracarboxylate (5). The splitting may be due to symmetric and antisymmetric coupling of the two C:O stretching vibrations or to their resonance coupling with an overtone. Analogous effects are observed for the nitrile frequency; its value in acetonitrile (15) is decreased slightly in going to butyronitrile (16), but increased by 12 cm.$^{-1}$ in ethyl cyanoacetate and 18 cm.$^{-1}$ in malonodinitrile (17). The difference in these last two figures agrees with the known stronger electron-attracting power of the nitrile group; this may also explain why the insulating effect of the extra methylene group is sufficient to prevent interaction of the two ester groups in diethyl succinate (4) while the C:N frequency in succinodinitrile (18) is slightly increased.

The unsaturated crotonic compounds show reduction in the respective frequencies compared with the saturated compounds of 20 cm.$^{-1}$ for the ester (6) and 27 cm.$^{-1}$ for the nitrile (20). This is due to the electromeric effect already described. An inductive effect can be transmitted by the olefinic bond so that the groups attached to the β-carbon atom have much the same effect as those on the α-atom. Rasmussen and Brattain (*loc. cit.*) pointed out that the small conjugation in ethyl ββ-diethoxyacrylate as shown by the smallness of the reduction in C:O frequency compared with that in saturated esters must be due to opposition by the inductive effect of the electrophilic ethoxy-groups to the mesomeric effect of the olefinic bond. A methyl group would be expected to show a smaller effect and in the opposite direction; the various acrylic and crotonic derivatives (6—8 and 19—22) show this effect by a lowering of the C:O or C:N frequency with methyl substitution. The electromeric effect also reduces the double-bond character of the C:C link itself, giving rise to a band at a lower position. The actual reduction in comparison to the hydrocarbon varies, but in each case it is about 18 cm.$^{-1}$ lower in the nitrile than in the corresponding ester, as would be expected from the higher electron-attracting power of the nitrile group.

Compounds in which more than one ester or nitrile group is attached to an olefinic bond must now be considered; it is this class about which little is known and which includes the ester-nitrile whose olefinic structure seemed to be contra-indicated by its C:O frequency.

First, let us take the case where two of these groups are on the same carbon atom. Then either may be conjugated with the C:C double bond, but not together because they are cross-conjugated. The fact that both are electron-attracting groups implies that the electron drift across the C:C bond must be shared between the two groups, so that although a greater drift would be expected to be caused by two groups than by one, the effect on individual substituent groups should be smaller. In accordance with this expectation, diethyl *iso*propylidenemalonate (9) has a lower C:C frequency by 14 cm.$^{-1}$, but a higher C:O frequency by 6 cm.$^{-1}$, than ethyl 3-methylbut-2-enoate (8). Similarly (1-ethylpropylidene)-malonodinitrile (23) has a lower C:C frequency by 46 cm.$^{-1}$ but a higher C:N frequency by 13 cm.$^{-1}$ than 3-methylbut-2-enonitrile (22); the frequencies observed for benzylidene-malonodinitrile (24) and its methyl derivative (25) are also in line with this effect. In the ester-nitriles, the resonance form with an ionic nitrile group must have a lower energy than that with an ionic ester group, because of the greater electron-attracting power of the former, and that form is therefore favoured. Consideration of ethyl 2-cyano-3-ethylpent-2-enoate (41) shows the competing effects of these two groups; compared with the diester (9) and the dinitrile (23), the C:O frequency is raised by 6 cm.$^{-1}$ and the C:N frequency is lowered by 10 cm.$^{-1}$, while the C:C frequency is intermediate between those of the unmixed compounds; compared with the monoester (8), the C:O frequency is raised by 12 cm.$^{-1}$, although still 22 cm.$^{-1}$ below that of the saturated ethyl cyanoacetate, while the C:N frequency is raised only 3 cm.$^{-1}$ compared with the mononitrile (22) and is 43 cm.$^{-1}$ below that in the saturated compound. Similarly, comparison of ethyl 2-cyanopent-2-enoate (40) with its related monoester (6) and mononitrile (20) shows the C:O and C:N frequencies to be increased by 13 cm.$^{-1}$ and 5 cm.$^{-1}$ respectively. The low C:C frequency in these asymmetric disubstituted compounds has already been noted; this band is also characterised by a high intensity, which would be expected from the high polarity of the bond induced by the two electron-attracting groups' being on the same carbon atom and therefore reinforcing one another.

When two of these groups are attached to opposite ends of the ethylenic bond, their electron-attracting properties will tend to polarise that bond in opposite directions. The resonance hybrid will be such that the oxygen or the nitrogen atom will be negatively charged and both olefinic carbon atoms positively charged; the separation of charge inherent in the ionic form of each polar group is therefore effectively relayed only to the α-carbon atom of the olefinic link and not to the β-atom as in the unsaturated mono-ester or nitrile. A higher ester-carbonyl or nitrile frequency would therefore be expected, and this is found. Examination of the *trans*-diesters, diethyl fumarate (10) and mesaconate (12) shows an increase of about 5 cm.$^{-1}$ in the C:O frequency above that in the appropriate monoester, while the *trans*-dinitriles (26) and (28) are increased about 10 cm.$^{-1}$ in their C:N frequency; in the *trans*-β-cyanocrotonate (42) the effect on the carbonyl frequency is slightly greater and on the nitrile frequency slightly less, a result which would be expected from the greater electron-attracting power of the nitrile group. These shifts are all comparable with those found in the asymmetrically disubstituted compounds, but the two classes differ as regards the intensity of the band due to the C:C bond. Compared with that of the monosubstituted compounds, its polarity is increased in the asymmetrically disubstituted compounds, but decreased in the symmetric ones (to zero in the completely symmetric compounds) so that the intensity of the band associated with its stretching is respectively increased and reduced. This effect occurs in both esters and nitriles, but the reduction is particularly noticeable in the latter, doubtless because the electron density is lower than in the esters.

The situation with the *cis*-disubstituted compounds is complicated by steric factors. An assessment of their importance has been made from a consideration of atomic models. In the *cis*-diesters, there would be considerable steric hindrance did not a non-planar structure obtain. The resultant reduction in conjugation increases the C:O frequency: thus, the absorption in diethyl maleate (11) is at 1734 cm.$^{-1}$, compared with 1727 cm.$^{-1}$ in diethyl fumarate, and is only 6 cm.$^{-1}$ below that in the saturated diethyl succinate; diethyl citraconate (13) is similarly 7 cm.$^{-1}$ above diethyl mesaconate in its C:O frequency. This effect has already been noted in the higher C:O frequency of diallyl maleate than in diallyl fumarate (Hampton and Newell, *loc. cit.*). In the dinitriles, there is no steric hindrance but the two nitrile groups are close to one another and, both being negatively charged, can be expected to repel one another. This leads to a more linear structure, a feature which should increase the conjugation of the olefinic bond with the nitrile groups, and so decrease the frequency of their stretching vibration. Four isomeric pairs of nitriles (26–27, 29–30, 32–33, and 34–35) have been examined and the C:N frequency in the *cis*-isomer appears to be about 5 cm.$^{-1}$ lower than in the *trans*-isomer; unfortunately, the band is split in two cases, so that any shift is masked. The slightly higher C:N frequency of 3 : 4 : 5 : 6-tetrahydro-*o*-phthalodinitrile (31) than in dimethylmaleidinitrile (30) may be due to the ring's opposing any change in bond angle resulting from steric repulsion. In the case of ethyl *cis*-β-cyanocrotonate (43) steric repulsion between the two polar groups should again occur, but in this case is most easily accommodated by a rotation of the ester group to a non-planar configuration. In agreement with this, the C:O frequency is 10 cm.$^{-1}$ above that in the *trans*-compound while the C:N frequency is at about the same position.

In the tetrasubstituted compounds all the factors must be considered together. Thus, in tetraethyl ethylenetetracarboxylate (14), the four ester groups are all tending to attract electrons and therefore oppose one another; further, they can only be sterically accommodated in a non-planar configuration. The result should be for the electronic state of the ester groups to be similar to that in the saturated ethyl ethanetetracarboxylate; this is so, for the C:O absorption, double in both cases, is only slightly lower in the unsaturated compound. In the diethyl dicyanoethylenedicarboxylate (44), the four polar groups are again in opposition; the ester groups are the weaker electron-attracting groups, and are, moreover, forced into non-planar configurations by steric repulsion from the nitrile groups so that the olefinic link must be conjugated mainly with the latter. The compound should therefore behave as unsaturated with respect to its nitrile groups, but saturated with respect to its ester groups. These considerations explain the high C:O frequency of 1750 cm.$^{-1}$, only 5 cm.$^{-1}$ lower than in the saturated ethane analogue (38), and the C:N frequency of 2229 cm.$^{-1}$ which is by contrast 30 cm.$^{-1}$ lower than in the ethane compound, and at about the expected position for an unsaturated nitrile. The low intensity of the C:C band is to be expected because the electronic distribution in the link is symmetrical and at a low level.

The conclusion to be drawn from these measurements and their interpretations is that great care should always be taken to allow for all possible effects when using infrared spectra in the elucidation of molecular structure. It has been shown that quite small effects, when cumulative, can lead to considerable shifts in characteristic frequencies in strongly polar molecules.

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CHESTER BEATTY RESEARCH INSTITUTE,
INSTITUTE OF CANCER RESEARCH: ROYAL CANCER HOSPITAL,
FULHAM ROAD, LONDON, S.W.3.

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