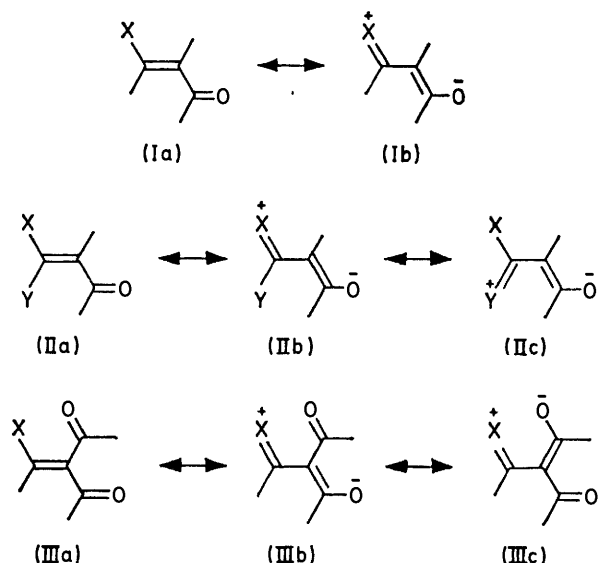


## The Vibrational Spectroscopy of Some Highly Conjugated Systems. Part 7.† Conformation and Electron Distribution in 1,1-Diacetylenes. The Phenomenon of Vanishing Raman Intensity for the Carbon Double Bond

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Previous studies on the i.r. and Raman spectroscopy of ethylenes oppositely substituted with one electron acceptor group and one or two donors are here extended to molecules containing two acceptors. Established criteria are used to assign conformation and, in particular, to decide the issue of coplanarity. In terms of this criterion, three such classes of molecule are identified: (1) both acyl groups coplanar with the carbon double bond; (2) *cis*-planar with *trans*-carbonyl out of plane, confined to molecules containing NH; and (3) the reverse *trans*-planar circumstance. Compounds of class (1) invariably possess an extremely low Raman intensity for the carbon double bond, even though this is usually strong in the i.r. spectrum. This is explained as almost total removal of mobile  $\pi$ -electron density from the carbon double bond, which does not however diminish the overall molecular dipole. It is concluded that conjugation, defined as bond equalisation, and resonance, resulting from charge sharing, are not synonymous for these molecules; the latter probably goes through a maximum as the degree of substitution increases.

THE remarkably low frequency and high intensity of the carbon double bond vibration when substituted at opposite ends by electron donor and acceptor groups, as in structure (I), has been the subject of considerable



research<sup>1-5</sup> since it first aroused comment some 30 years ago.<sup>6</sup> We have demonstrated that, if such compounds are to be regarded as substituted enones, it is possible to derive rules which will predict carbonyl and carbon double bond frequency according to the nature of these substituent groups and their precise alignment one to the other.<sup>4,5</sup> These rules have proved to be remarkably additive even when a second electron donor is present, as in structure (II).<sup>5</sup> We now turn our attention to the opposite circumstance: molecules that contain two electron acceptors acting together, as in structure (III).

The fall in both double bond frequencies on  $\beta$ -substitution into a simple enone is readily understood in terms of

(Ib), and the still greater contribution of dipolar canonical forms to (II) correctly predicts the further fall in frequency brought about by two electron donors. The same qualitative argument applied to (III) produces a different result. While carbon double bond frequency should likewise fall in comparison to (I), that of carbonyl should rise somewhat, so enhancing the expected frequency separation. That is the first strand in the argument.

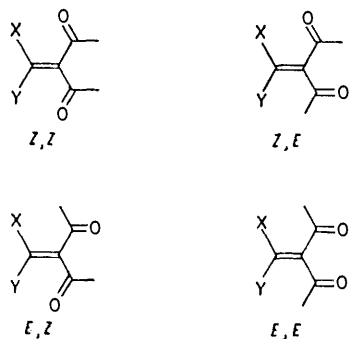
We have shown<sup>4</sup> that  $\nu_{C=O}$  and  $\nu_{C=C}$  for classes (I) and (II) are strongly coupled, possessing in large measure the character of antisymmetric and symmetric vibrational modes respectively (nevertheless, we shall continue to use  $\nu_{C=O}$  and  $\nu_{C=C}$  as a convenient form of shorthand). While these arguments remain valid, coupling between the two carbonyls now intrudes as an extra possibility. As with the coupling of  $\nu_{C=O}$  to  $\nu_{C=C}$  it is possible that the mutual alignment of these groups will affect the nature and extent of this coupling. In Scheme 1 we indicate the four possible planar alignments (three, if the groups X and Y are identical). Also in Scheme 1 we list the carbonyl frequencies and intensities of some imides of known conformation in the solid state. The *Z,Z*-conformation is exemplified by *N*-methylglutarimide (1)<sup>7</sup> (we avoid five-membered rings because of bond angle complications). Here coupling takes place to give symmetric and antisymmetric modes, the second much the stronger, at a frequency separation of 55  $\text{cm}^{-1}$  in the solid state. A similar separation is found for dipropionylimide (2), known from its crystal structure<sup>8</sup> to possess the *E,E*-conformation. Here however the symmetric mode is the stronger, a predictable consequence of the parallel alignment of the carbonyl groups. The same intensity pattern is shown by open-chain anhydrides, which also tend to prefer the *E,E*-conformation.<sup>9</sup> Most imides take up the *Z,E*-conformation shown by diacetylimide (3), in which normal co-ordinate analysis demonstrates little coupling to occur; the 1736 and 1701  $\text{cm}^{-1}$  carbonyl bands are dominated by the *Z*- and *E*-vibrational modes respectively.<sup>10</sup> This lack of coupling is probably responsible for the higher mean

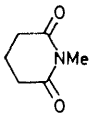
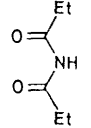
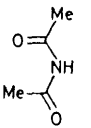
† Previous Parts in this series have been titled The Infrared Spectroscopy of Some Highly Conjugated Systems. Part 6, P. J. Taylor, *Spectrochim. Acta*, 1978, **34A**, 115.

frequency but lower frequency separation than elsewhere shown by this compound. We contend that these frequency separations and relative intensities (not, of course, the frequencies themselves) may give some idea of what to expect for the corresponding alignments of structure (III). If so, the *E,E*-conformation should be recognisable on sight, but the others may be more difficult to distinguish. That is the second strand in the argument.

All this assumes planarity. In fact planarity, though favoured by conjugation, may often be difficult to attain for steric reasons to do with the substituent on carbonyl or the size of the donor group X (or Y). Hence one carbonyl or both may lie out of plane, or alternatively the whole molecule may twist along the axis of the carbon double bond. In addition charge repulsion may specifically disfavour the *E,E*-conformation, which is likely therefore to be rare, and may operate in other cases also. Space-filling models suggest that the *Z,E*-conformation will, more often than not, optimise these factors. That is the third strand in the argument.

Three patterns appear to predominate among the

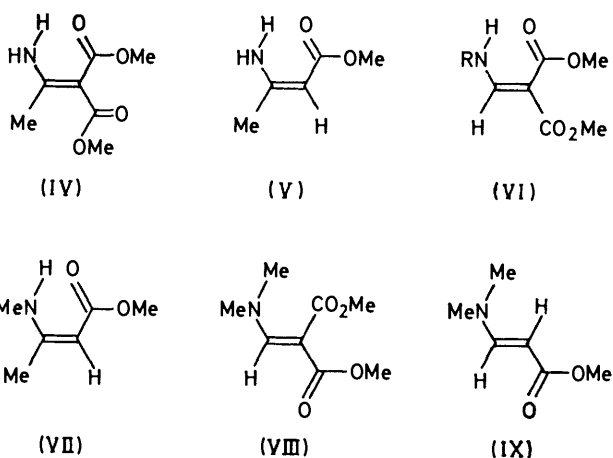


	$\nu_{C=O}/\text{cm}^{-1}$	Mean $\nu/\text{cm}^{-1}$	$\Delta\nu/\text{cm}^{-1}$
 (1)	1727 <sub>ms</sub> 1672 <sub>s</sub>	1700	55
 (2)	1740 <sub>vs</sub> 1681 <sub>m</sub>	1710	59
 (3)	1736 <sub>m</sub> 1701 <sub>vs</sub>	1719	35

SCHEME 1

compounds we have investigated so far. Some show a further sharp drop (40–80  $\text{cm}^{-1}$ ) in carbon double bond frequency when compared with the nearest related structure, experimental or theoretical,<sup>5</sup> of type (I) or (II). An example later to be discussed is the diester (IV), whose  $\nu_{C=O}$  at 1519  $\text{cm}^{-1}$  compares with that for (V) at

1564  $\text{cm}^{-1}$ . Elsewhere for the most part their i.r. characteristics approximate to those of a type (I) or (II) compound with an extra carbonyl band at higher frequency. There are two typical patterns within this class. Where NH is present, the model structure most



closely approximated possesses the *cis-cis* alignment<sup>4</sup> with respect to NH and carbonyl.\* For example, the carbonyl and carbon double bond frequencies of (VII) at 1652 and 1611  $\text{cm}^{-1}$  respectively are reflected in bands at 1665 and 1613  $\text{cm}^{-1}$  for (VI), with *trans*-carbonyl at 1694  $\text{cm}^{-1}$ . In all other cases this pattern is reversed: frequencies and intensities fit for *trans*-conjugation, so presumably the *cis*-carbonyl is that forced out of plane. This is certain for (VIII), as demonstrated by its crystal structure;<sup>12</sup> *cis*-carbonyl frequency is at 1724  $\text{cm}^{-1}$  with the other two relevant bands, at 1694 and 1614  $\text{cm}^{-1}$ , very close to those for (IX).<sup>12</sup> Such a contrast between these sub-classes is consistent with previous studies<sup>1-3</sup> on enamino-ketones which have shown the *trans*-configuration to be favoured except where a strong intramolecular hydrogen bond can be formed. In some cases this clean contrast is blurred, probably by some degree of non-planarity for both carbonyls, and perhaps some twisting of the carbon double bond. In addition some compounds give mixtures of conformers, or one in solution and another in the solid state; again, this has precedent.<sup>4,5</sup>

In this paper we examine a number of type (III) compounds in the light of the contrasting and often conflicting criteria sketched out above. Their structures are very diverse, which while it adds generality to the argument, notably complicates its presentation. As previously<sup>4,5</sup> we have made extensive use of solvent studies, not only to identify the separate bands due to each conformer where mixtures exist, but also in more subtle ways. In particular we exploit our discovery<sup>5</sup> that the slope of a plot of  $\nu_{C=C}$  versus  $\nu_{C=O}$  as a function of solvent, designated *S*, can be used as an index of conjugation. Also as previously,<sup>4</sup> we have used deuteration as an

\* As previously<sup>3-5</sup> we define *cis* and *trans* relative to the best electron donor present; in i.r. terms this order is  $^5\text{N} \gg \text{CON} > \text{S}$ , i.e. the  $\sigma_{\text{R}}^{\ominus}$  order.<sup>11</sup>

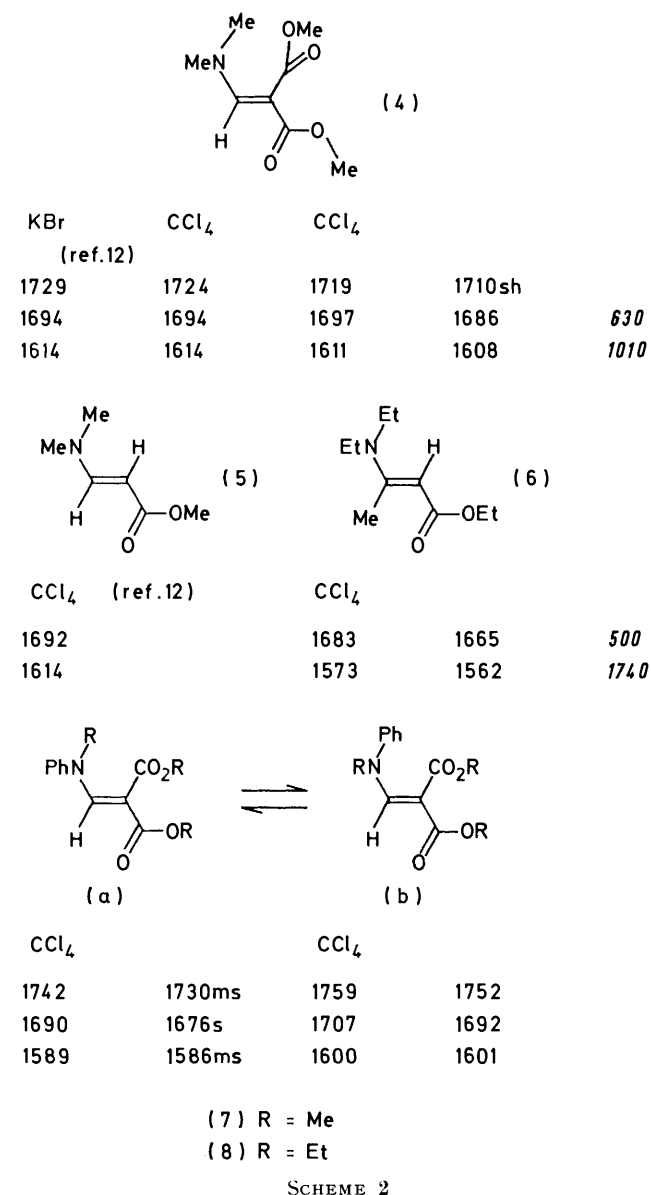
aid in band assignments. The full solvent shift data are contained in Supplementary Publication No. SUP 22552 (19 pp.).\* Here we quote only those that are strictly pertinent. As before<sup>4,5</sup> we use chloroform as our standard solvent for predictive purposes, and all data in the text or the Schemes (other than Raman) refer to chloroform solutions unless otherwise qualified.†

It will be convenient to argue from the known to the unknown, from the simple to the complex, and from compounds which closely resemble some established structure to those that do not. That is the nearest approach to a logical order we can find for our presentation.

*Simple trans-Planar Compounds.*—Schmueli *et al.*<sup>12</sup> find the alignment shown in Scheme 2 for the crystal structure of (4),<sup>13</sup> with *cis*-carbonyl twisted at 68° to the plane formed by the other double bonds. The near-equivalence in i.r. frequency between the solid state and solution is sufficient evidence that this alignment is preserved.<sup>12</sup> Its carbon double bond and lower carbonyl frequencies are virtually identical to those of (5);<sup>12</sup> nevertheless the upper carbonyl frequency, rather below that expected for a simple ester,<sup>14</sup> indicates some vestigial *cis*-conjugation. That this is obtained at the cost of some *trans*-conjugation, *i.e.* some degree of twisting occurs in solution, is suggested by the comparison with (6).<sup>4</sup> Some part of the rise in carbon double bond frequency is probably due to the substitution of hydrogen for methyl, on the exact effect of which we have insufficient evidence, but some, perhaps half, may be due to loss of planarity. The data for (8)<sup>15</sup> support this. An analogue (7) has been shown<sup>13</sup> to exist as the mixture of conformers indicated, with (7a) predominating. Two unequal conformers are visible in the i.r. spectrum of (8), the less favoured possessing higher double bond frequencies all round. Comparison of either with (4) or (6) suggests better *trans*-conjugation for (8) with a corresponding loss in conjugation by *cis*-carbonyl. This is presumably due to the greater bulk of the substituents on nitrogen. At the same time, there is evidence that the amino-group is perfectly planar in neither conformer (the n.m.r. data of Shvo and Shanan-Atidi<sup>13</sup> throw no light on this) as might reasonably result from its greater bulk. This evidence consists in the marked loss (unquantified) of carbon double bond intensity relative to (4) and (6). Such a loss is to be expected wherever the donor atom cannot enter fully into conjugation; intensity is more sensitive than frequency to this, as in u.v. spectroscopy,<sup>16</sup> whereas the reverse is true for conjugation to carbonyl.<sup>4,5</sup> The same information is conveyed by the drop in *S*, which is 0.68 for (6)<sup>4</sup> and *ca.* 0.4 for (4) but probably not above 0.2 in (8a). Strictly speaking *S* is an index of coupling not of conjugation, but for a given conformer the two tend to run in parallel.<sup>4,5</sup>

*NH-Containing 1,1-Diacyl-2-aminomethylenes.*—Compounds (9) and (10) may be regarded as *cis*-planar analogues to the *trans*-planar examples (4) and (8) described

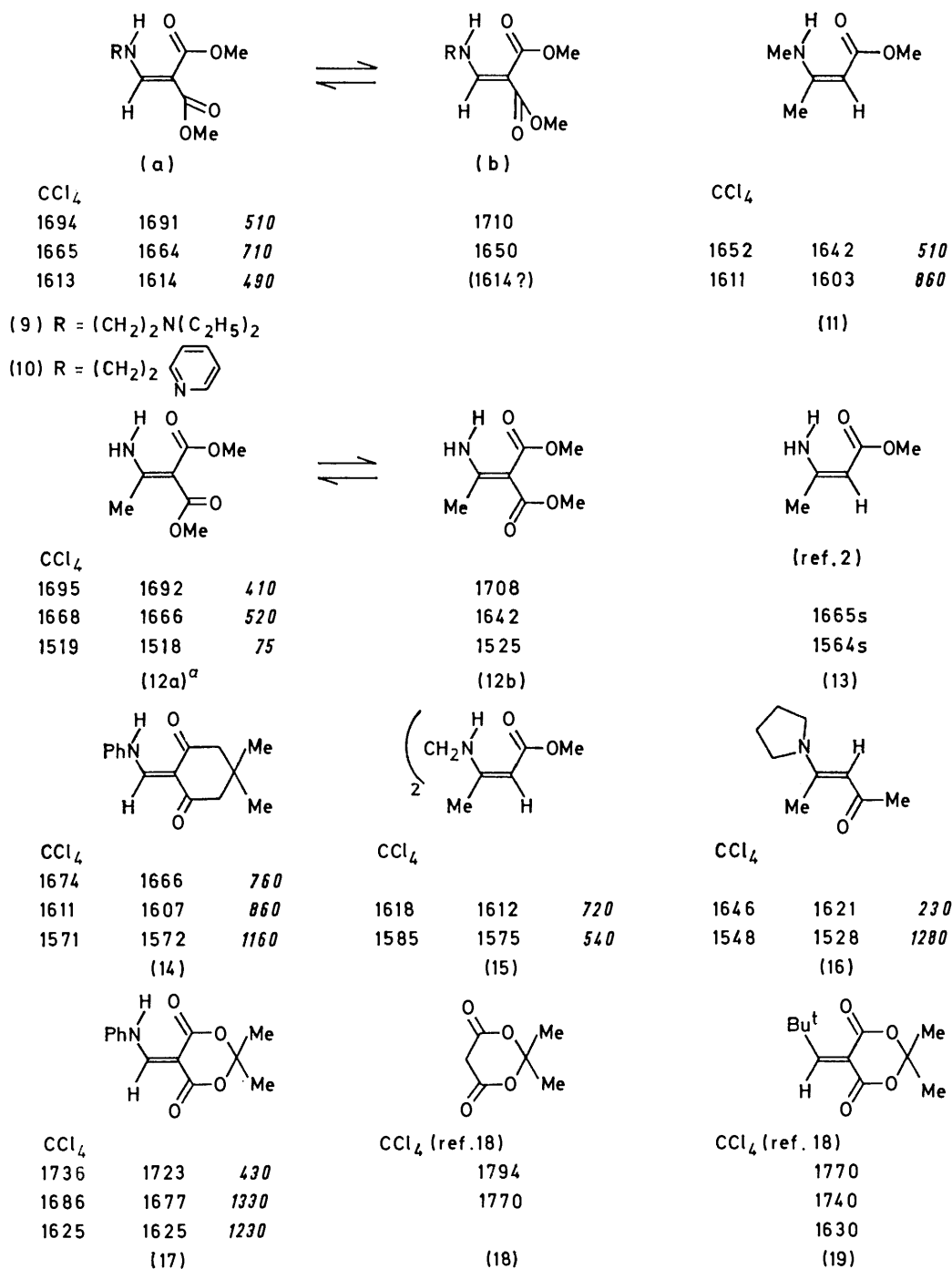
above. Data for (9) appear on Scheme 3; those for (10) are very similar. A major and a minor conformer co-exist; their close resemblance suggests the same configuration and we account for them as shown. The frequency difference between their upper carbonyl bands is



consistent with a *transoid* and a *cisoid* conformation respectively.<sup>4,17</sup> The latter (b) is the more crowded, so accounting, by a compression effect, for the lower frequency of its *cis*-carbonyl. Partial conjugation by *trans*-carbonyl is shown by its own relatively low frequency, and by the higher frequency of *cis*-carbonyl when compared to the monoester (11).<sup>4</sup> The near-

† In Schemes 2—5 we attempt a rough representation of the molecular alignments that are known or believed to occur; lack of any indication for COR implies severe non-planarity. Frequency (cm<sup>-1</sup>) appears in Roman figures, intensity ( $\epsilon_A$ ) in italics. An Arabic number key is used for actual compounds, a Roman number key for idealised part-structures. Frequency predictions for the latter (in CHCl<sub>3</sub>) are based on ref. 5.

\* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.



SCHEME 3 <sup>a</sup> Intensity values are minima since the proportion of (12b) is appreciable

identity in frequency of  $\nu_{C=O}$  as between (9) and (11) may in part result from the different effects of hydrogen and alkyl as  $\beta$ -substituents; cf. (5) and (6).

It is useful to compare the primary amino-derivative (12), which also possesses two conformers (most probably the same two) but has all the hallmarks of a fully planar molecule, such as a very low carbon double bond vibration relative to the monoester (13).<sup>2</sup> The low intensity of this band poses a problem.\* For simple enaminones and aminocrotonates the intensity of  $\nu_{C=C}$  is a

simple function of the N...O separation; it is therefore higher for *trans*- than for *cis*-compounds and highest of all in the *trans-s-trans* alignment.<sup>4</sup> In simpler, less conjugated molecules such as  $\alpha,\beta$ -unsaturated ketones,  $\epsilon_A(C=C)$  contrariwise is higher for the *s-cis* conformer, the

\* Deuteriation studies<sup>2-5</sup> have shown that, in primary and secondary aminoenones, considerable coupling takes place between this band and the NH deformation mode, as well as with carbonyl. That coupling is also found here. Nevertheless this band is sufficiently well behaved in respect of its frequency and intensity variations for the following argument to be unaffected.

result of greater vibrational coupling<sup>4</sup> (in the more complex case this factor is over-ridden). We have some preliminary evidence<sup>5,17</sup> that type (I) and (II) compounds in which the resonance donor properties of the heteroatoms X or Y are for some reason attenuated tend to revert to the above 'less conjugated' pattern, and the same effect, for steric reasons, has been noted for (8) above. We postulate that excessive electron withdrawal may have much the same effect on carbon double bond intensity as insufficient electron donation, by reducing electron density at the centre of the conjugated system. If so, the presence of two planar acyl groups in place of one, while it will lower carbon double bond frequency [*cf.* (III)], should also lower its intensity unless a further reserve of electron density becomes available. This is unlikely in the present case since, as we have demonstrated,<sup>4</sup> aminocrotonates already show induced electron donation by the nitrogen atom relative to enamino-ketones. Some confirmatory evidence can be adduced from the sharp reduction in *S* and overall solvent shift for (9), (10), and (12) relative to (11); we have shown solvent shift to correlate quite well with the overall 'electron richness' of the molecule.<sup>4</sup> Further applications of this principle will follow, including evidence from Raman spectroscopy (*vide infra*).

The ease with which these compounds attain planarity clearly depends on the amino-group in the order  $\text{NH}_2 > \text{RNH} > \text{R}_2\text{N}$ , *i.e.* that expected in terms of steric bulk. The other rule to note is the preferred *Z*-conformation of the in-plane carbonyl (this seems general for aminocrotonates<sup>3,4,17</sup>) balanced by the less planar carbonyl in such a way that the *Z,E* alignment is attained or approached.

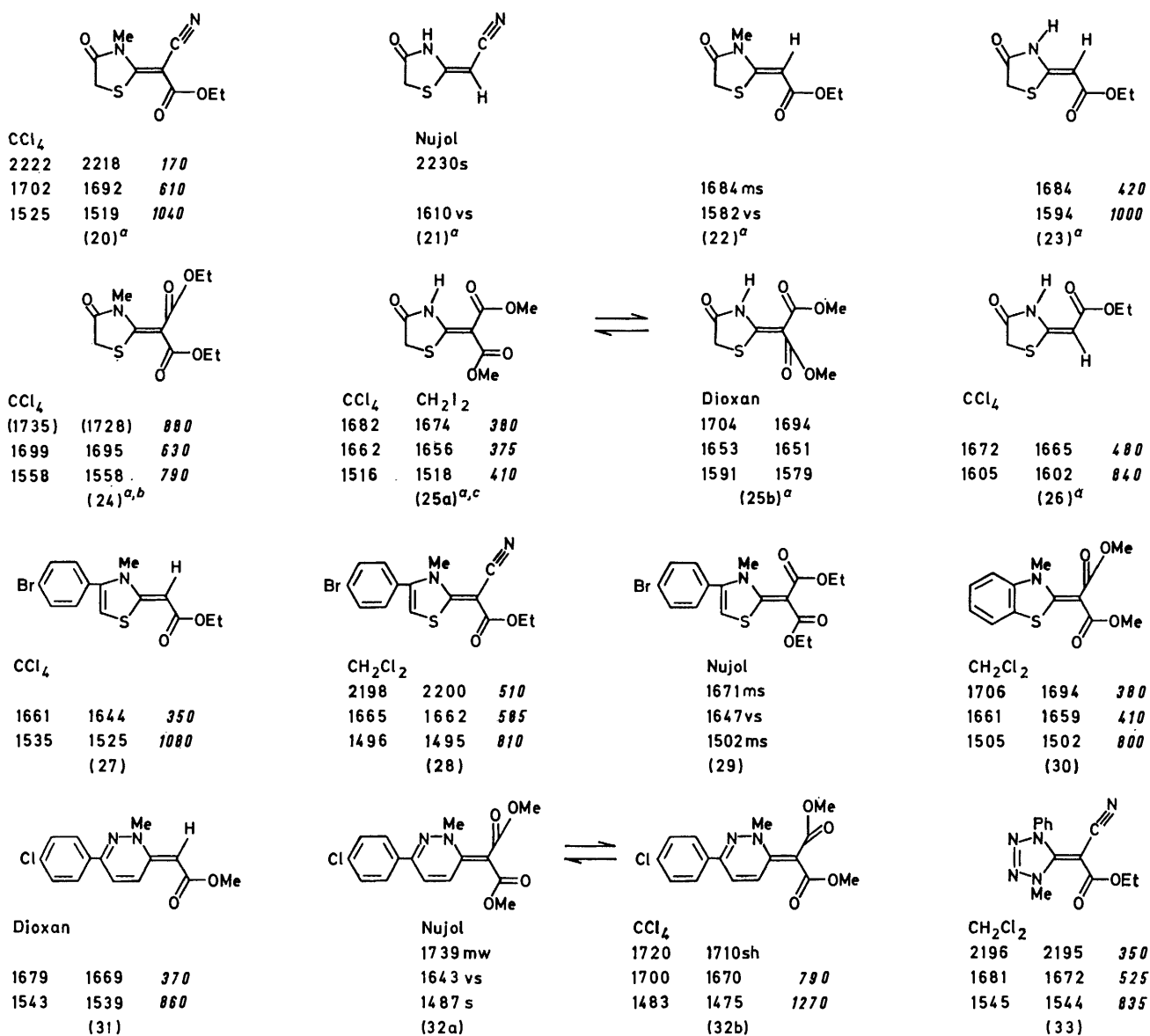
The cyclic diones (14)<sup>18</sup> and (17)<sup>19</sup> were originally chosen for study as putative examples of the planar *Z,Z* alignment. This is clearly not the case. Comparison of  $\nu_{\text{C}=\text{C}}$  in each case with the corresponding modes of (15) and (16) and of (6) and (11) respectively<sup>4</sup> shows each to lie close to the higher alternative, and not to represent a notable drop in frequency as in (12). In fact as for (9) and (10) a real drop may be present when the difference in expectation suggested by (5) and (6) is allowed for, but not as much as would be anticipated for true planarity (*vide infra*). It is notable that carbon double bond intensity, like its frequency, lies close to the higher value provided by each pair of exemplars. In the light of the above discussion one possibility that suggests itself is some twisting of both carbonyls out of the plane of the carbon double bond while the nitrogen atom remains in full conjugation. On the evidence that  $\epsilon_{\text{A}}(\text{C}=\text{C})$  is less reduced, this is more severe for (14). Supporting evidence comes from the carbonyl frequencies. While the lower in each case is essentially that bonded to NH, as is also consistent with their relative intensities,<sup>4</sup> their separation appears excessive on this ground alone and the explanation probably lies in coupling. From the dioxans (18) and (19) studied by Bihlmayer *et al.*<sup>19</sup> and typical figures (20  $\text{cm}^{-1}$ ) for carbonyl separation in  $\beta$ -diketones<sup>20a</sup> we estimate  $\Delta\nu$  20–30  $\text{cm}^{-1}$  for the

expected effect of this coupling in (14) and (17); note that this is a good deal less than for the imide (1). Added to the carbonyl frequency difference between (6) and (11) this gives an estimated  $\Delta\nu$  value of *ca.* 50  $\text{cm}^{-1}$  for (17) if each carbonyl group is equally conjugated to nitrogen. The corresponding figure for (14) is <40  $\text{cm}^{-1}$ . These calculations fit for (17) but the gap for (14) is excessive. We conclude therefore that (14) approaches the condition of *cis*-planarity with *trans*-carbonyl more out of plane, as is consistent with its much stronger intramolecular hydrogen bond ( $\nu_{\text{NH}}$  is at 3 000 as against 3 200  $\text{cm}^{-1}$ ), whereas conjugation in (17) is better balanced. Note incidentally that the exceptionally high carbonyl frequencies of (17) are reflected by (18) and (19) where they lie much above the normal value for a  $\gamma$ -lactone.<sup>14</sup> This may be due to the unusual nature of the alkoxy-group, which is so structured that each ester function acts as an electronegative substituent with respect to the other; the 5-methyl derivative of (18) is a remarkably strong acid,  $\text{p}K_{\text{a}}$  4.77.<sup>21</sup> To this extent, (6) and (11) are inadequate models and more extensive cross-comparison is not justified.

*Heterocyclic Anhydro-bases.*—Cyanoacetate derivatives such as (20) are valuable for calibration purposes, since they are expected to exhibit type (III) characteristics and co-planarity may safely be assumed. Shvo and Shanani-Atidi<sup>13</sup> find a number of simple examples of this class to prefer the *cis*-cyano-*trans*-ester configuration. Bearing in mind the known<sup>3</sup> thermodynamic preferences of (21) and (22) as displayed in Scheme 4, we have no hesitation in suggesting for (20) and its analogues the overall alignment shown.

Comparison of (20) with (21) and (22) shows the modest rise in  $\nu_{\text{C}=\text{O}}$  and large fall in  $\nu_{\text{C}=\text{C}}$ , by 70  $\text{cm}^{-1}$  compared to their mean, to be expected on our argument. We attribute the lack of reduction in  $\epsilon_{\text{A}}(\text{C}=\text{C})$  to induced electron donation. This is brought about in (20) by the presence of a second donor group [*cf.* the discussion above concerning the very low  $\epsilon_{\text{A}}(\text{C}=\text{C})$  value of the simple amino-derivative (12)]. Surprisingly, this intensity falls in (24) relative to (20) despite the clear evidence from carbon double bond and upper carbonyl frequency that (24) is not fully planar. The explanation probably lies in the less effective resonance acceptor properties of nitrile than of alkoxycarbonyl;<sup>11</sup> it is resonance and not inductive effects that regulate carbon double bond intensity in compounds of this type.<sup>5,22</sup> Comparison of (28) with (30), where the same situation probably obtains (*vide infra*), makes the same point. Where two ester groups are coplanar, as in (25a) and (29) and still more in (12), the reduction in  $\epsilon_{\text{A}}(\text{C}=\text{C})$  is severe.

On the evidence taken together, (24) is a *trans*-planar molecule with a not too badly twisted *cis*-carbonyl. It might be anticipated that only a small reduction in steric hindrance, such as involved in the replacement of NMe by NH, would suffice to allow planarity. In fact, the major conformer of (25) has all the appearance of a fully planar molecule, with  $\nu_{\text{C}=\text{C}}$  *ca.* 85  $\text{cm}^{-1}$  below the mean of (23) and (26).<sup>5</sup> On the evidence of these exemplars, its



SCHEME 4 <sup>a</sup> For the sake of clarity, the frequency of ring carbonyl is omitted. <sup>b</sup> The uppermost frequency is superimposed on that of ring carbonyl, hence its anomalous intensity value. <sup>c</sup> Intensity values are minima since the proportion of (25b) is appreciable

1656 and 1674  $\text{cm}^{-1}$  bands are assigned to *cis*- and *trans*-carbonyl respectively. A compression effect leading to a stronger intramolecular hydrogen bond, as in (9b) and (12b), will explain why the lower band lies below that for (26). Its 1674  $\text{cm}^{-1}$  band also falls, relative to (20) and (24). We account for this in terms of a switch to the *s-trans* conformation, for which a fall of *ca.* 25  $\text{cm}^{-1}$  in carbonyl frequency is expected.<sup>4,5</sup> If so, the sterically favoured *Z,E* alignment results for (25a). The strong preference among these compounds for the *s-cis* conformation,<sup>3,5,17</sup> which steric factors here over-ride, may however explain the existence of the minor conformer (25b). With  $\nu_{\text{C}=\text{C}}$  at 1579  $\text{cm}^{-1}$ , this is clearly not a planar molecule. Most probably it is *cis*-planar with its *trans*-ester function arranged in a *cisoid* conformation. Its double bond frequencies show highly

irregular solvent shifts, evidence probably for variations in angle of twist as a function of solvent.

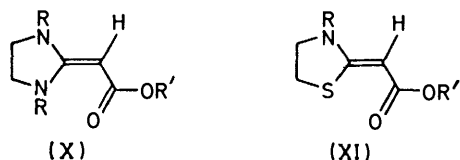
The thiazolines (27)—(30)<sup>17</sup> show exceptionally strong donor properties, as is evidenced by their very low frequency carbon double bond vibrations even in monoacyl derivatives, and solvent shifts which, where the comparison can be made, exceed those for the thiazolidinones (20)—(26). The nitrile (28) shows, relative to (27), precisely the changes to be expected for the alignment shown. So does the diester (29) if, as in (25a), a switch to the *trans-s-trans* conformation accounts for the fall in *trans*-carbonyl frequency relative to (28). The low frequency of the upper carbonyl band and relatively low intensity of the carbon double bond vibration also indicate planarity. Again, the sterically favoured *Z,E* alignment results; all diacyl derivatives of whose *cis*-

planarity we are reasonably certain appear to be of this type.

The upper carbonyl frequency position and the relative intensities of the other two double bond vibrations enable (30) to be assigned as a *trans*-planar molecule with a twisted, probably *s-cisoid*, *cis*-carbonyl group. It will be noted that (29) and (30) possess almost identical carbon double bond frequencies despite their differences in alignment. This is the fortuitous result of increased conjugation in (29) cancelling against a switch to the *s-trans* conformation, for which a rise of *ca.* 15 cm<sup>-1</sup> is predicted.<sup>5</sup> Incorporation of this correction leads to a 'real' drop of *ca.* 40 cm<sup>-1</sup> in  $\nu_{C=C}$  between (27) and (29), comparable to that between (13) and (12) and a good deal more convincing than the apparent difference.

The pyridazine diester (32) exists as two conformers. That with the highest and lowest frequencies is found in the solid state, whereas the other, with two intermediate frequencies, predominates in solution and in the most polar solvents is the only one. We postulate a *trans*-planar structure for each with the *cis*-ester group not far out of plane. Both pairs of carbonyl frequencies, and those of the carbon double bond, then show the differences expected<sup>4</sup> for the conformational change shown. The only apparent anomaly, which however would be still more difficult to explain on any other alignment, concerns the considerable rise in  $\epsilon_A(C=C)$  relative to (31). On the evidence of large values for *S* and overall solvent shift, (31) possesses a strongly donating heterocyclic ring,<sup>17</sup> and this is still true of (32b) as will be seen. Its very sharp drop (by 60 cm<sup>-1</sup>) in  $\nu_{C=O}$  relative to (31), despite less than perfect conjugation by *cis*-carbonyl, is further evidence for induced electron donation. The rise in  $\epsilon_A(C=C)$  is similar to that found between (16) and (6), which originates in the same way.<sup>4</sup>

We possess no simple exemplars with which (33) may be compared, but the alignment shown may be assumed on steric grounds. It is instructive to compare (33) with the model part-structure (X), for which double



bond frequencies of 1 615 and 1 525 cm<sup>-1</sup> can be calculated.<sup>5</sup> The corresponding calculation for (XI) gives 1 645 and 1 540 cm<sup>-1</sup>. Comparison of these values with those found (in chloroform) for (33) and (28) respectively gives a deviation in mean frequency of 38 and -14 cm<sup>-1</sup> (we have demonstrated<sup>4,5</sup> that the mean is a more reliable index of conjugation than either frequency separately). While introduction of nitrile must influence this figure [as for (28) relative to (27) it does] both compounds should be equally affected, so that the above deviations are still significant in a relative sense. On our previous evidence<sup>17</sup> they should reflect the comparative electronegativity of the heterocyclic moieties; con-

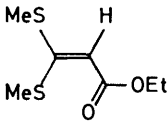
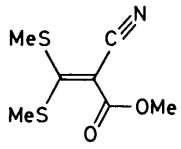
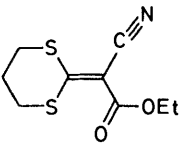
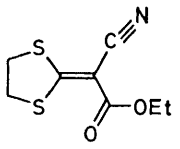
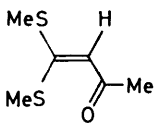
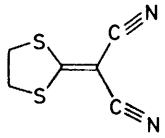
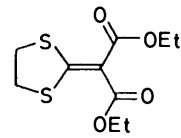
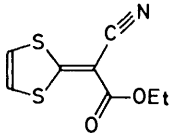
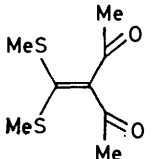
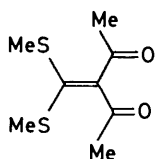
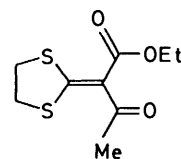
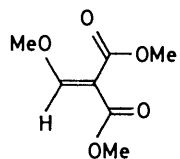
sistently, tetrazole is more electronegative than thiazole.<sup>23</sup> The above argument assumes coplanarity for each; on the evidence of high and similar double bond intensities, no major difference is likely in this respect.

*Sulphur and Oxygen Analogues.*—The dialkyldithio-derivatives (34)—(43) have been extensively investigated and their spectra discussed, by Jensen and Henriksen<sup>24</sup> and by Sandström and Wennerbeck,<sup>25</sup> who report their i.r. data for KBr discs and chloroform solution respectively. Since these media appear almost equivalent in their effect on i.r. frequency,<sup>5</sup> their data are directly comparable with one another's and with our own. Pertinent results are assembled in Scheme 5.

The effect of nitrile in (35)<sup>25</sup> relative to (34)<sup>5</sup> is entirely in line with expectation, with a rise of 28 cm<sup>-1</sup> and a fall of 73 cm<sup>-1</sup> in  $\nu_{C=O}$  and  $\nu_{C=C}$  respectively. It is not clear why the latter should rise again (by 22 cm<sup>-1</sup>) in (36), unless the six-membered ring constrains the sulphur atom orbitals at a suboptimal angle for conjugation. The slight rise in  $\nu_{C=C}$  for (37) relative to (36) approaches the 20 cm<sup>-1</sup> predicted<sup>5</sup> for a five-membered ring. The intensity of the carbon double bond vibration is unchanged in (36) relative to (34) and in (37) it increases, as is often the case for *carbonyl* in five-membered rings.<sup>26</sup> The continued high intensity of  $\nu_{C=C}$  in (36) [that for (35) is unfortunately not given<sup>25</sup>] has two probable origins. The first is the reduced resonance acceptor property of nitrile relative to alkoxy-carbonyl, referred to in the preceding section; this is consistent with its very sharp drop in the diester (40). The other is the considerable ability of sulphur to undergo induced electron donation, presumably the result of its high polarisability, and discussed above in connection with the thiazolidinone (20). Nevertheless, cross-comparison of carbon double bond intensity between (37), (20), and (28), clearly shows that nitrogen is a better electron donor *per se* than sulphur even when acylated, consistently with our past conclusions.<sup>5</sup> Comparison between the band intensities for (28) and the qualitative data of Jensen and Henriksen<sup>24</sup> for (41) brings out the same point. The latter shows the drop in  $\epsilon_A(C=C)$  relative to (37) which one might expect as a result of cross-conjugation in the dithiole ring.

The diester (40) has all the i.r. characteristics expected for a planar molecule with both carbonyl groups fully in conjugation. Jensen and Henriksen<sup>24</sup> and Sandström and Wennerbeck<sup>25</sup> both note that two carbonyl frequencies appear in this and related formally symmetric molecules. The latter authors postulate in explanation an *s-cis-s-trans* arrangement of the ester groups. Detailed analysis confirms this. Their frequency separation of 33 cm<sup>-1</sup> is close to theory<sup>5</sup> (25 cm<sup>-1</sup>), while their relative intensity is also that expected [*cf.* (3)]. On the evidence of (19) the *Z,Z*-alignment cannot be ruled out entirely, but on steric grounds [*cf.* the analysis for (17)] it seems unlikely. Again, (40) shows the same type of cross-relation in its i.r. characteristics to (25a)\* and (29)

\* The intramolecular hydrogen bond of (25a) must be allowed for in this comparison.

			
CCl <sub>4</sub>	(ref. 25)	Dioxan	Dioxan
1696 1681 395	2204	2214 2216 170	2217 2216 140
1532 1528 545	1709	1703 1700 420	1701 1695 410
(34)	(35)	(hidden) 1477 550	(1487) 1490 655
		(36)	(37)
			
(ref. 25)		CCl <sub>4</sub>	KBr (ref. 24)
1640	2216 280	1722 1709 290	2205s
1480	1482 310	1686 1676 440	1675s
(38)	(39)	1493 1487 240	1470m
		(40)	(41)
			
Nujol	CCl <sub>4</sub>	KBr (ref. 24)	CCl <sub>4</sub>
1688s	1696 1690 430	1704vs	1739 1726s
1673s	1664 1657 325	1630s	1718 1706sh
1544m	1486 1481 240	1406vs	1643 1635ms
(42a)	(42b)	(43)	(44)

SCHEME 5

as (37) does to (20) and (28); this result could scarcely come about by accident.

The highly anomalous solid-state i.r. spectrum of the diketone (42)<sup>25</sup> can be explained in terms of its crystal structure,<sup>27</sup> which shows each carbonyl group to be twisted at an angle of 65° to the plane of the carbon double bond. The result is a highly twisted *E,E*-conformation in which the acyl groups subtend an angle of 109° to one another. Poor conjugation therefore accounts for the high carbon double bond frequency [*cf.* (38)<sup>25</sup>] while the mutual alignment of the acyl groups gives rise to the almost zero coupling responsible for nearly coincident carbonyl frequencies of equal intensity. Its quite different solution i.r. spectrum is equally anomalous. This is the only compound of formally symmetrical structure we have examined whose upper carbonyl frequency is stronger than the lower one (*cf.* Figure 4 of ref. 27). This is consistent with the *E,E*-conformation [*cf.* (2)]; a closer approach to this in solution than in the solid state will plausibly explain the spectroscopic differences. On the evidence of (43)<sup>24</sup> which by comparison with (40) probably exists in the alignment shown, it seems likely that  $\nu_{C=O}$  for (42b)

would be considerably lower were it to exist in the *Z,E*-conformation as suggested by Sandström and Wennerbeck.<sup>25</sup> Our proposed conformation for (43) follows<sup>4</sup> from the large fall in frequency and lesser intensity of its lower, *i.e.* *E*-carbonyl, relative to (40). It may be relevant to (40) and (43) that acyl groups seem to possess a greater tendency than alkoxycarbonyl to take up the *s-trans* conformation.<sup>4</sup>

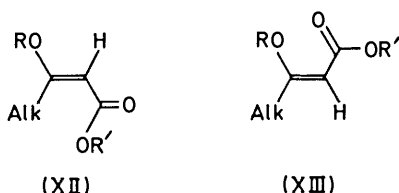
The synthetic reagent dimethyl methoxymethylene-malonate (44) is the only other compound in this set for which the upper carbonyl band is stronger than the lower. That might suggest the *E,E*-conformer, but in fact we prefer an approximation to the *Z,E*-conformation as shown on Scheme 5. Of the four planar enamino-ketone alignments, the *cis-s-cis* gives much the strongest carbonyl vibration;<sup>4</sup> this is still true of the planar diester (12), where hydrogen bonding makes it the lower band. This factor is absent in (44), where accordingly the *cis*-carbonyl is expected at the higher frequency: for the model structures (XII) and (XIII) we predict<sup>5</sup> carbonyl frequencies (for chloroform solution) at 1680 and 1710 cm<sup>-1</sup> respectively. The actual frequencies are naturally higher, but *relative* frequencies, as well as



intensities, are compatible with the model. Both model structures predict about  $1630\text{ cm}^{-1}$  for  $\nu_{\text{C}=\text{C}}$ ; as in (4) and (9), this near-agreement with the observed frequency probably results from a fortuitous cancellation between a fall due to limited extra conjugation and a rise due to the substitution of hydrogen in (44) for the alkyl group assumed in the model of frequency prediction.

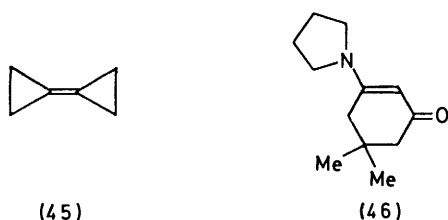
**Raman Spectroscopy.**—The carbon double bond vibration is expected to be very strong in the Raman spectrum, because of its pool of highly mobile  $\pi$ -electrons.<sup>20b</sup> The only published case of zero intensity, for the class of bicyclopopylidenes (45), is attributed to a much reduced polarisability resulting from its abnormal bond angles.<sup>28</sup>

In several of the compounds whose Raman spectra we have examined, the carbon double bond vibration



almost *disappears*. It is absent from (17), just detectable in (12), (29), and (39), and present in (4), (14), and (46) but at much reduced intensity relative to its i.r. equivalent. Only in (23) and (42a) can it be described as a strong vibrational mode. Results are summarised in the Table.

Despite failure to obtain Raman spectra for a number of key compounds because of strong fluorescence, a consistent pattern emerges from these results. Strong Raman carbon double bond vibrations are confined to compounds which contain two donor groups: either set against one in-plane acceptor as in (23), or two but both badly twisted as in (42a). With one electron donor, intensity is always much less. It remains stronger than carbonyl in the *trans*-planar diester (4) and the twisted



diketone (14), but in the planar *trans-s-trans* amino-enone (46) whose alignment corresponds to maximum conjugation,<sup>4</sup> these intensities have reversed. In all compounds with two planar acceptors, intensity dwindles to vanishing point. This is equally true for one donor in (12) or two in (29) and (39), and is even found for the appreciably non-planar but highly polarised diester (17) with its single donor group. The most striking contrast is provided by (42a) and (39), where the donor atoms are identical and whose whole difference revolves round acceptor group planarity. One would like more results,

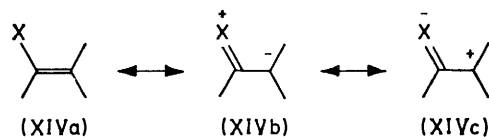
especially for intermediate categories like (20), (24), and (28) and possible ultimates such as (25), but these are among the failures.

From this and our previous<sup>3-5,17</sup> i.r. and Raman studies, it is possible to build a consistent picture of the electron distribution in these compounds which is nevertheless in some respects surprising. We begin with the simplest exemplars. Enamines possess<sup>29</sup> strong double bond vibrations near  $1650\text{ cm}^{-1}$  which, therefore, show

I.r. (Nujol) and solid-state Raman frequencies			
Compound	I.r., $\nu/\text{cm}^{-1}$	Raman, $\Delta\nu/\text{cm}^{-1}$	Assignments
(4)	1 726ms	1 721w	<i>cis</i> - $\nu_{\text{C}=\text{O}}$
	1 688ms	1 696m	<i>trans</i> - $\nu_{\text{C}=\text{O}}$
	1 606sbr	1 601ms	$\nu_{\text{C}=\text{C}}$
(12)	1 675ms	1 682s	<i>trans</i> - $\nu_{\text{C}=\text{O}}$
	1 659s	1 651m	<i>cis</i> - $\nu_{\text{C}=\text{O}}$
	1 510m	1 507vw	$\nu_{\text{C}=\text{C}}$
(14)	1 669s	1 658m	<i>trans</i> - $\nu_{\text{C}=\text{O}}$
	1 590vsbr	1 602m	<i>cis</i> - $\nu_{\text{C}=\text{O}}$
		1 571ms	$\nu_{\text{C}=\text{C}}$
(17)	1 728ms	1 729mw	<i>trans</i> - $\nu_{\text{C}=\text{O}}$
	1 680vs	1 687mw	<i>cis</i> - $\nu_{\text{C}=\text{O}}$
	1 634s	Absent	$\nu_{\text{C}=\text{C}}$
(23) <sup>a</sup>	1 724s	1 735m	ring $\nu_{\text{C}=\text{O}}$
		1 712m	
	1 665s	1 659vw	<i>trans</i> - $\nu_{\text{C}=\text{O}}$
(29)	1 568vs	1 570vs	$\nu_{\text{C}=\text{C}}$
		1 556s	
	1 671ms	1 665m	<i>cis</i> - $\nu_{\text{C}=\text{O}}$
(39)	1 647vs	1 643m	<i>trans</i> - $\nu_{\text{C}=\text{O}}$
	1 502ms	1 505w	$\nu_{\text{C}=\text{C}}$
	2 215sh	2 216m	$\nu_{\text{C}\equiv\text{N}}$
2 206s	2 204w		
(42a)	<sup>b</sup>	1 487vw	$\nu_{\text{C}=\text{C}}$
	1 688s	1 688ms	$\nu_{\text{C}=\text{O}}$
	1 673s	1 675sh	
(46) <sup>c</sup>	1 544m	1 544s	$\nu_{\text{C}=\text{C}}$
	1 604s	1 608vs	$\nu_{\text{C}=\text{O}}$
	1 561s	1 546ms	$\nu_{\text{C}=\text{C}}$

<sup>a</sup> I.r. data from ref. 3. <sup>b</sup> Hidden by Nujol; strong band in solution (*cf.* Scheme 5). <sup>c</sup> I.r. data from ref. 4.

little change in frequency compared to the unsubstituted molecule; quantitative intensities have not been reported but extrapolation from Katritzky's results<sup>22</sup> suggests  $\epsilon_{\text{A}}(\text{C}=\text{C})$  in the range 200–300.  $\alpha\beta$ -Unsaturated ketones show frequencies at  $1640$ – $1620\text{ cm}^{-1}$  and intensities generally less than the above except in the *s-cis* conformation, where coupling is maximised.<sup>4</sup> Here Raman intensity is very high.<sup>30</sup> This rather striking difference between electron donors and (some) acceptors relates to the presence of multiple bonds in the latter. Polarisation of (XIV) in the sense of (XIVb) or



(XIVc) will happen only to a limited extent unless one of these charges can be blended away. This is possible in (XIVc) when X is carbonyl or nitrile, and still more effective in (Ib) where both charges are dispersed. Hence enamines, enones, and compounds of type (I), show successively lower carbon double bond frequencies. Still further falls are predicted for types (II) and (III)

and these, as seen above, are realised for planar molecules.

The above treatment rationalises frequency shifts in a qualitative manner, some part of which is capable of quantitative treatment.<sup>5</sup> It is, however, only part of the story; we have also to consider intensity. Here the critical intensity is  $\epsilon_A(\text{C}=\text{C})$ , which because of coupling tends to reflect the importance of polar canonical forms such as (IIb).<sup>4</sup> The intensity of an i.r. mode relates, not to the dipole as such, but to its *change* in the course of the vibration. A small dipole that changes a lot may in principle give rise to the same i.r. intensity as a large dipole which changes little. The high dipole of an enamine may not alter much on vibration since polarisation in the sense of (XIVb) is restricted. The similar i.r. intensity found for enones results, perhaps fortuitously, from a smaller actual charge separation multiplied by a larger overall charge spacing<sup>20c</sup> and reinforced, in a conformationally dependent manner,<sup>4</sup> by vibrational coupling. In type (I) compounds all these factors come together in long and highly polarised dipoles capable of resulting in enormous carbon double bond intensities.\* For simple enamino-ketones, we have shown<sup>4</sup> that  $\epsilon_A(\text{C}=\text{C})$  is an almost linear function of the  $\text{N} \cdots \text{O}$  dipolar separation.

Thus far we could have used conjugation,† in its sense of bond order equalisation, or resonance,† in its sense of charge sharing, as terms equally suited to describe the sequence of falling double bond frequency and rising intensity found in enamines, enones, type (I) compounds, and most of type (II). At this point, these concepts part company. Planar type (III) compounds show further falls in frequency at the side of their type (I) or (II) analogues, but intensity no longer rises. In fact, it generally falls. Raman spectroscopy provides the essential clue. Raman intensity depends on the magnitude of the induced dipole that can be generated in the course of a molecular vibration;<sup>20d</sup> for double bonds, therefore, it will be critically dependent on the motion of the most polarisable electrons present, *i.e.* the  $\pi$ -electrons. It is high in simple ethylenes (it should be very high in enamines, but these have not been studied). It is still high in enones, where polarisation is limited. It is *less* even in simple enamino-ketones such as (46) because the presence of an electron donor to share the

\* A referee has pointed out that this argument, and the corresponding argument concerning Raman intensities below, depends on the assumption of similar vibrational amplitudes, since these intensities vary with  $(\partial\mu/\partial r)^2$  and  $(\partial\alpha/\partial r)^2$  respectively. Nevertheless the observation described in the following sentence could not have been made were not this assumption substantially correct in that case. The same is true for Katritzky's finding of a correlation between  $(\sigma_R^\ominus)^2$  and double bond intensity.<sup>22</sup> It may of course fail elsewhere, but it is difficult to see how the very consistent picture we have been able to discern could survive large and random failures. The existence of self-compensating errors in otherwise naive assumptions is well known as a prime condition of survival for extra-thermodynamic treatments generally.<sup>31</sup> However, we recognise that 'with enough variables one can fit an elephant,' and the ultimate validity of our thesis will have to depend on its predictive value outside the charmed circle of compounds, however much varied, considered in this paper.

positive charge [compare (Ib) with (XIVb)] has vastly increased electron transfer and a good deal of this electron density now resides on carbonyl, whose Raman intensity rises, with correspondingly less in the carbon double bond. The extent of this polarisation is partly a matter of alignment; (4) appears to be less polarised than (46). The addition of a second electron donor as in (23) restores electron density and, with it, Raman intensity; i.r. intensity also benefits but not by so much, probably because, in the presence of a single acceptor, neither donor exerts its full effect.<sup>5</sup> (Katritzky and his co-workers<sup>22</sup> find intensities to be additive in 1,1-disubstituted ethylenes, but these are mostly simple vibrations, not coupled as here; it is *frequencies* that appear to be additive in our case.<sup>5</sup>) Two planar acceptor groups denude the carbon double bond of  $\pi$ -electrons almost entirely; this leads to near-zero Raman intensity even in the presence of two electron donors. I.r. intensity may still be strong since the molecular dipole is now very large and only quite a small change in it is required for an intense vibration. The extent of this change depends on the alignment of carbonyl and the efficacy of the donor atoms. Once polarisation has gone to extremes and no further increase in dipole can take place during the vibration, even i.r. intensity must vanish; this may be the state approached by (12).

A picture emerges according to which, while conjugation as defined above is a continuous function of the number of donor and acceptor groups inserted, resonance may go through a maximum. Amino-enones such as (46) are nicely in balance and their resonance energies are probably quite high. This may well remain true for more complex molecules such as (23) and (27). With (25) and (28) the imbalance is beginning, and for (12) it is extreme. In such cases, most of the mobile electron density is concentrated in the carbonyl groups; there is little left anywhere else. Since the resulting molecular dipole is high, i.r. intensity holds up till quite a late state in this process, creating a misleading impression of high conjugation which the Raman intensities correct. Obviously complications enter to muddle this simple picture, to do with the relative efficacy of donor atoms, induced electron donation, carbonyl group conformation and departures from planarity, all as discussed above, but as a framework for the facts it seems to hold.

Solvent shifts are also relevant here. It has been shown<sup>4</sup> that overall solvent shift for  $\nu_{\text{C}=\text{O}}$  plus  $\nu_{\text{C}=\text{C}}$  taken together is related to 'electron richness,' with the relative shift of  $\nu_{\text{C}=\text{C}}$  versus  $\nu_{\text{C}=\text{O}}$  within this total, defined as *S*, a conformationally dependent quantity. Both are very large for (16) and (46), somewhat less for the amino-crotonates (6) and (11) where polarisation has begun,

† These definitions are helpful in this context but are not intended to pre-empt their different usage elsewhere. We use such terms with unease, but can find no way to avoid them. Another such is 'electron richness,' our usage of which is prompted by the absence of any all-embracing quantitative substitute. This point is emphasised by recent evidence<sup>32</sup> suggesting that no additive  $\sigma$ -type relations exist for the  $\pi$ -excessive heterocycles, a class possessing some electronic features in common with the compounds described here.

and little changed in their nearest available type (II) analogues,<sup>5</sup> but very much reduced in most planar compounds of type (III). Since solvent shifts are probably mediated largely by the lone pair electrons on carbonyl,<sup>4</sup> which are not those mainly responsible for i.r. or Raman intensity, there is no certainty that these phenomena relate to the same cause, but their rough parallelism is of interest.

*Conclusions.*—When this work began, we hoped to derive for type (III) compounds the kind of predictive rule already successfully applied<sup>5,17</sup> to those of types (I) and (II). This aim has not been realised. Nevertheless, there are compensations. In the first place, we have established criteria which should enable the conformations of many type (III) compounds to be established with reasonable certainty, starting with no more information than their i.r. and Raman double bond frequencies and intensities and those of a simpler type (I) or (II) exemplar. The latter need not even be known provided that its frequencies can be calculated.<sup>5</sup> For such molecules, the usual n.m.r. methods are often inapplicable. In the second place, we have been led to a deeper understanding of the electron distribution in these molecules and the way in which their i.r. and Raman characteristics monitor this. Future publications will extend these insights to the oxo-heterocycles.

#### EXPERIMENTAL

*Materials.*—Compounds (4),<sup>13</sup> (8),<sup>15</sup> (12),<sup>33</sup> (14),<sup>18</sup> (17),<sup>19</sup> (25),<sup>34</sup> (36),<sup>24</sup> (37),<sup>35</sup> (39),<sup>36</sup> (40),<sup>37</sup> and (42)<sup>38</sup> were prepared by the published procedure, whereas the preparation of (20),<sup>3</sup> (24), and (25) was carried out according to the method of Satzinger<sup>39</sup> with appropriate choice of starting material. Compound (44) was a commercial sample. Preparative details of the remaining compounds studied are incorporated into SUP 22552. All compounds were checked by n.m.r. for identity and purity before use.

Compounds related to (14) have been shown in the literature as the alternative hydroxy-imino tautomer;<sup>40</sup> however, the amino-oxo form given on Scheme 3 has been established by a definitive n.m.r. study.<sup>41</sup> In no other compound discussed is tautomeric ambiguity likely.

*Spectroscopy.*—I.r. spectra were run on a Perkin-Elmer 457 double grating, double beam i.r. spectrometer, Raman spectra as solid samples on a Cary 83 Raman spectrometer using the 488 nm exciting line (heavily fluorescent samples were tried with all available exciting lines, but without success). Details of the i.r. methodology were as published.<sup>4</sup> Full i.r. spectroscopic details on all compounds studied are given in SUP 22552.

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