317. *The Molecular Structure of Some Products from the Ehrlich–Sachs Reaction.*

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Several families of compounds, obtained as products of Ehrlich–Sachs-type reactions (reactive methylene compounds and aromatic nitroso-compounds), have been studied in solution by infrared spectroscopy. Deductions regarding the molecular structure of these compounds have been made. Several absorptions which occur at abnormal infrared frequencies are discussed.

The Ehrlich–Sachs reaction, *i.e.*, the base-catalysed condensation of a reactive methylene compound with an aromatic nitroso-compound, has been the subject of recent investigations,[1,2] and the characteristic absorptions in the infrared spectra (obtained for mulls) of typical series of Ehrlich–Sachs products have been reported.[2]

(I) *p*-NMe$_2$·C$_6$H$_4$·N:C(CN)·CO$_2$Et *p*-Me·NH·C$_6$H$_4$·N:C(CN)·CO$_2$Me (II)

In some of the series, striking variations in the absorptions given by homologous compounds were observed. Thus *N*-(α-cyano-α-ethoxycarbonylmethylene)-*N'N'*-dimethyl-*p*-phenylenediamine (I) gave a carbonyl absorption at 1740 cm.$^{-1}$, whereas its methoxy-analogue absorbed at 1708 cm.$^{-1}$. Moreover, *N*-(α-cyano-α-methoxycarbonylmethylene)-*N'*-methyl-*p*-phenylenediamine (II) existed in three crystalline modifications, (*a*) maroon needles, m. p. 170° (from methanol), $\nu_{\text{C:O}}$ 1687 cm.$^{-1}$, (*b*) yellow-orange needles, m. p. 170° (from benzene), $\nu_{\text{C:O}}$ 1713 cm.$^{-1}$, and (*c*) dark red prisms with blue fract, m. p. 168° (from the benzene mother-liquor), $\nu_{\text{C:O}}$ 1733 and 1706 cm.$^{-1}$.

These and certain other features of the spectra obtained indicated that the compounds merited further examination. Analytical specimens of the various series of compounds were kindly placed at our disposal for this purpose by Professor F. Bell, who has described their method of preparation.[1,2]

Experimental.—A Hilger H800 spectrophotometer fitted with a sodium chloride prism was used. Calibration was effected with reference to pyrrole vapour (3530 cm.$^{-1}$), polystyrene film (3029 and 2923 cm.$^{-1}$), dichloroacetonitrile (2261 cm.$^{-1}$), and acetone vapours (1742 cm.$^{-1}$), and is believed to be accurate to ± 10 cm.$^{-1}$ in the N–H$_{\text{st}}$ absorption region, ± 5 cm.$^{-1}$ in the C:N absorption region, and ± 2 cm.$^{-1}$ for carbonyl absorptions. Solutions in carbon tetrachloride or in chloroform (0·005—0·02M) were examined in a matched pair of variable-path-length cells fitted with sodium chloride windows. Solvent absorptions were removed by compensation in the reference beam. Absorptions are quoted as cm.$^{-1}$.

Ehrlich–Sachs Dinitriles.—Table 1 gives the cyano-absorption frequencies of *N*-dicyanomethylene-*N'N'*-dialkyl-*p*-phenylenediamines as solids and as 0·01M-solutions in chloroform. (Certain of the mull absorptions previously given [2] are corrected.)

Table 1. *Cyano-absorptions of* 4,2,1-RR'N·C$_6$H$_3$R''·N:C(CN)$_2$.

R	R'	R''	C:N (mull)	C:N (solution)
Me	Me	H	2216, 2197	2227, 2212sh
Me	Et	H	2212, 2202sh	2224, 2211sh
Et	Et	H	2213 (1 peak only)	2223, 2209sh
Me	Me	Me	2214, 2198	2221, 2210sh
Et	Et	Me	2214, 2198	2223, 2210sh

Space-filling models of these molecules show that the two cyano-groups exist in markedly different environments, as illustrated by (III), the least steric hindrance being given when

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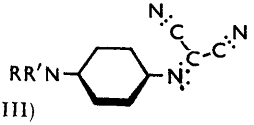
[1] Bell, *J.*, 1957, 516.

[2] Anderson and Bell, *J.*, 1959, 3708.

the $-N:C(CN)_2$ group is perpendicular to the plane of the benzene ring. The cyano-group lying in close proximity to the benzene ring will be subject to interaction with the π-electron cloud. Despite non-planarity of the molecule, the cyano-group remote from the benzene ring can be conjugated to the latter by interaction of the ring π-cloud, N atom lone-pair, N:C π-cloud and C:N π-cloud. It is therefore proposed that the cyano-group remote from the benzene ring absorbs at 2210 ± 2 cm.$^{-1}$, the cyano-group in close proximity to the ring absorbing at 2224 ± 3 cm.$^{-1}$. The validity of these deductions is supported by the behaviour in solution of the Ehrlich–Sachs esters discussed below.



(III)

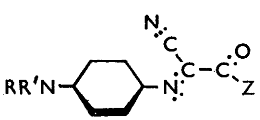
Table 1 shows that the presence of a methyl group in the 2-position of the ring (R'' in Table 1) does not alter the absorption frequency of either cyano-group, although greater steric hindrance to free rotation is created. A study of models, however, shows that the configuration which departs least from planarity and so has the greatest stability is given when the cyano-group and the hydrogen atom in the 6-position are in close proximity. The preferred molecular configuration will, therefore, not be changed by introduction of a methyl group into the 2-position. This effect also applies to the other series of compounds discussed in this paper.

Ehrlich–Sachs Esters.—Table 2 lists the cyano and carbonyl absorption frequencies of *N*-(α-cyano-α-alkoxycarbonylmethylene)-*N'N'*-dialkyl-*p*-phenylenediamines (R' = Me, Et) and of *N*-(α-cyano-α-alkoxycarbonylmethylene)-*N'*-alkyl-*p*-phenylenediamines (R' = H) as mulls and as 0·005M-solutions in carbon tetrachloride.

TABLE 2. *Cyano- and carbonyl absorption of* $4,2,1\text{-}RR'N{\cdot}C_6H_3R''{\cdot}N:C(CN){\cdot}CO_2R'''$.

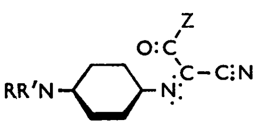
					C:N		C:O	
R	R'	R''	R'''		Mull	Soln.	Mull	Soln.
Me	Me	H	Me		2220	2212	1708	1757, 1731
Me	Me	H	Et		2200	2213	1740	1754, 1724
Et	Et	Me	Et		2200	2207	1694	1750, 1722
Et	H	H	Et	orange	2220	2211	1750	1756, 1726
				maroon	2202		1726	
Me	H	H	Me	orange	2210	2216	1713	1760, 1733
				maroon	2198		1687	
Et	H	H	Me		2210	2214	1731	1760, 1733
Me	H	H	Et		2215	2216	1741	1756, 1727

The marked variations in both the carbonyl and the cyano-absorption frequencies given by mulls disappear when the compounds are studied in solution, which give two carbonyl bands. The low and constant single absorption (2211 ± 5 cm.$^{-1}$) of the cyano-group indicates, in terms of the deduction already made concerning cyano-groups, that of the two possible geometrical isomers (IV) and (V) the latter is preferentially formed under the reaction conditions used.[1]



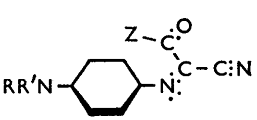
(IV) Z = OR'''

(IX) Z = NH$_2$



(V) Z = OR'''

(VII) Z = NH$_2$



(VI) Z = OR'''

(VIII) Z = NH$_2$

The occurrence of a single C:O frequency in the solids and of two in the solutions is clear evidence that the molecules can exist as rotational isomers, as represented by (V) and (VI).

Models show that whilst rotation can take place about the C–CO_2R''' bond, no free rotation is possible about the N–ring bond. In (V), the carbonyl group is in close proximity to the π-cloud of the benzene ring, and the resulting interaction will raise the carbonyl frequency. (An α-activated αβ-unsaturated ester would be expected [3] to give absorption in the range 1735—1750 $cm.^{-1}$.) In (VI), the OR''' group is in close proximity to the π-cloud of the benzene ring. This will result in an increased contribution from the $R'''O^{+}{:}C{-}O^{-}$ polar canonical form to the carbonyl absorption. This resonance form may be further stabilised by interaction of the opposed formal charges on the carbonyl-oxygen atom and the closely adjacent carbon atom of the cyano-group. Thus the carbonyl frequency of isomer (VI) should be considerably lower than that of (V); the assignments of 1755 ± 5 and 1725 ± 5 $cm.^{-1}$ can be made to (V) and (VI) respectively.

Temperature-dependence measurements were made to investigate the relative stabilities of the two isomers (V) and (VI) for each member of the series. In every case the intensity of absorption of the 1725 $cm.^{-1}$ band increased with temperature. Isomer (VI) is therefore the less stable form.[4] The fact that the more stable form is that in which the opposition of like charges is greater has been previously discussed,[4] but is apparently not yet fully understood.

The variations in the carbonyl absorptions of the solids can be attributed to the fixation of one or other isomer, consistent with the production of the lattice of lowest energy. Two of the compounds studied (see Table 2) were isolated in two crystal forms. Use of a Kofler hot-stage microscope showed that in each case one of the forms was unstable, having a transition temperature below the true melting point at which it irreversibly changed, accompanied by a change in colour and crystal structure, to the more stable crystallographic form. Thus the maroon form of *N*-(α-cyanoethoxycarbonylmethylene)-*N'*-ethyl-*p*-phenylenediamine changed at 86° to the orange form (m. p. 107°); for *N*-(α-cyanomethoxycarbonylmethylene)-*N'*-methyl-*p*-phenylenediamine the orange form changed at 158° to the maroon form (m. p. 170°). Infrared studies of the temperature-dependence of these two compounds showed that, at the transition temperature, two carbonyl absorptions were given, one of which slowly decreased in intensity as the temperature was gradually raised, finally leaving the other as a single band. When the compound eventually melted, the two bands reappeared.

These examples of rotational isomerism support the initial assignments to the cyano-frequencies in Ehrlich–Sachs dinitriles: if the assignments be reversed, leading to (IV) in place of (V), models show that, although rotational isomerism of the ester group is still possible, an explanation of the large differences in the two carbonyl absorptions can no longer be found.

Ehrlich–Sachs Amides.—0·01M-Solutions in chloroform of several *N*-carbamoylcyanomethylene-*N'N'*-dialkyl-*p*-phenylenediamines all showed a cyano-band at 2211 ± 3 $cm.^{-1}$. The assignment for cyano-groups therefore favours the structure (VII), or its possible rotational isomer (VIII), rather than (IX). In the carbonyl absorption region, bands were present at 1694 ± 2 (s), 1618 ± 1 (s), and at 1555 (w) and 1495 (s). When each compound was studied in a range of solvents of varying polarity,[5] the 1694 $cm.^{-1}$ band varied between 1710 $cm.^{-1}$ (CCl_4) and 1691 $cm.^{-1}$ ($CHBr_3$), whilst the other three bands remained constant. A dν/ν plot (based on carbon tetrachloride) for the 1691—1710 $cm.^{-1}$ band against acetophenone [5] gave a straight line. Hence only one carbonyl band is given in solution, the 1618 $cm.^{-1}$ band being attributed to the N:C bond. Rotational isomerism, although feasible on steric grounds, is therefore not exhibited by these amides.

It is well known that the contribution of the polar canonical form $H_2N^{+}{:}C{-}O^{-}$ in amides is considerable, and is responsible [3] for occurrence of the carbonyl absorption normally

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[3] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1958, 2nd edn., pp. 179, 205.

[4] Bellamy, Thomas, and Williams, *J.*, 1956, 3704.

[5] Bellamy and Rogasch, *Spectrochim. Acta*, 1960, **16**, 30.

near 1690 cm.$^{-1}$ for dilute solutions. An α-activated αβ-unsaturated amide would also be expected to give a carbonyl band near 1690 cm.$^{-1}$. The observed 1691—1710 cm.$^{-1}$ band, therefore, indicates that an activation effect on the carbonyl group is tending to reduce the $H_2N^+{:}C{-}O^-$ contribution: this effect would be given in structure (VII), on the basis of the reasoning in the discussion of Ehrlich–Sachs esters. Structure (VIII) would involve increased contribution by the form $H_2N^+{:}C{-}O^-$, leading to an absorption frequency much lower than that normally exhibited by amides. It is concluded that in structure (IX) the charge-distribution effects become so great that this isomer is unstable.

The compound *N*-carbamoylcyanomethylene-*N'N'*-di-n-propyl-*p*-phenylenediamine [1] was, however, found to give two carbonyl bands at 1714w and 1657s cm.$^{-1}$ in the solid state. For the liquid state and for chloroform solution only one band at 1694 cm.$^{-1}$ was given. Repeated purification failed to yield material in which the 1714 cm.$^{-1}$ band was absent from the solid-state spectrum. Identical spectra were given by crystals grown from different solvents and from cast films: the possibility of the presence of dimorphic crystal forms is therefore small. The cause of this effect was not determined. A similar crystal effect was given by *N*-(α-cyano-α-methoxycarbonylmethylene)-*N'*-methyl-*p*-phenylenediamine (II) (see Table 2); on one occasion a third isomer, strongly crystalline and giving absorptions at 1733m and 1706m cm.$^{-1}$, was obtained. On melting, the compound crystallised as the stable yellow-orange isomer, giving absorption at 1713 cm.$^{-1}$. Numerous recrystallisation attempts failed to yield any further quantity of the third isomer, which would appear to have been formed by the simultaneous crystallisation of both rotational isomers.

Condensations involving 2 Mols. of Cyanoacetic Esters and Condensations between Dinitriles and Esters.—These respectively produce *N*-(2-cyano-1,2-dialkoxycarbonylvinyl)-*N'N'*-dialkyl-*p*-phenylenediamines and *N*-(1,2-dicyano-2-alkoxycarbonylvinyl)-*N'N'*-dialkyl-*p*-phenylenediamines [2] (see Table 3a and b respectively). It was suggested [2] on infrared evidence that these contained an N–H group; this has now been confirmed by alkaline hydrolysis to the corresponding *NN*-dialkyl-*p*-phenylenediamines, which were characterised as their acetyl and benzoyl derivatives.[6]

When both series of compounds were studied as mulls, their characteristic NH, CN, and CO frequencies were little influenced by the nature of the alkyl groups. For each series, the variation between compounds is shown in Table 3.

Each compound in the two series was then studied in solution (0·01M) in each of the following solvents: carbon tetrachloride, methylene chloride, chloroform, diethyl ether, nitromethane, and bromoform. The NH and CO frequencies of each varied little with change of solvent; Table 3 shows the maximum frequency shift given by any of the compounds of each series.

TABLE 3. *Solid and solution spectra:* (a) 4,2,1-$RR'N{\cdot}C_6H_3R''{\cdot}NH{\cdot}C(CO_2R'''){:}C(CN){\cdot}CO_2R'''$, (b) 4,2,1-$RR'N{\cdot}C_6H_3R''{\cdot}NH{\cdot}C(CN){:}C(CN){\cdot}CO_2R'''$

	N–H			C⋮N		C:O					
	Mull *	Soln.*	Solvent † vartn.	Mull *	Soln.*	Mull *	Soln.*	Solvent † vartn.	Mull *	Soln.*	Solvent † vartn.
(a)	3275 ±20	3215 ±10	±5	2228 ±8	2222 ±5	1755 ±5	1755 ±5	±7	1675 ±5	1675 ±5	±2
(b)	3235 ±35	3220 ±20	±10	2222 ±12	2220 ±5	—	—	—	1688 ±6	1678 ±6	±3
				(1 peak only)							

* ±x = limits of variation between compounds in the series.
† Max. frequency shift of any compound when examined in solvents of differing polarities.

In these compounds, the low frequencies of the N–H absorption and of a carbonyl

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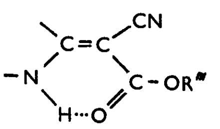
[6] McKusick, Heckert, Cairns, Coffman, and Mower, *J. Amer. Chem. Soc.*, 1958, **80**, 2806.



(A)

absorption suggest the existence of strong intramolecular hydrogen bonding. Models show that group (A) (inset) forms a compact six-membered ring system; the frequency 1675 cm.$^{-1}$ is therefore assigned to this ester group. The variation of this band in different solvents is small, ± 3 cm.$^{-1}$ (Table 3); this is consistent with strong intramolecular hydrogen bonding, which prevents normal interaction of proton-donating solvents with the C:O link.[7] The second ester group (1755 cm.$^{-1}$) in series (a) (Table 3) suffers severe steric hindrance and is almost 90° out of plane with respect to the C:C bond. The absorption frequency observed is therefore more typical of a saturated ester than of an $\alpha\beta$-unsaturated ester (cf. ref. 8).

The Colour of N-(*2-Alkoxycarbonyl-*1,2-*dicyanovinyl*)-N′N′-*dialkyl-*p-*phenylenediamine.*—These compounds lack extended conjugation but are dark red. Solutions in chloroform showed a broad band with $\lambda_{max.}$ 453 mμ. A study of very dilute solutions (5×10^{-4} to 5×10^{-5}M) in chloroform in 1—10 mm. quartz cells showed that the intensity of the 453 mμ band decreased rapidly with decreasing concentration, whilst a new band ($\lambda_{max.}$ 346 mμ) increased in intensity. The spectra exhibited an isosbestic point at 394 mμ; two species were therefore present in solution.

To investigate this effect, a series of tricyanovinylanilines, $R{\cdot}C_6H_4{\cdot}NH{\cdot}C(CN){:}C(CN)_2$, was prepared,[6] where R = H, Me, Et, Pr^i, Bu^t, OMe, and NMe$_2$. The series therefore had increasing electron-donation from the R groups in the *para*-position. The series ranged in colour from pale yellow for R = H to orange for R = OMe, but the R = NMe$_2$ compound was deep maroon. The yellow series had $\lambda_{max.}$ ranging from 348 mμ for R = H to 362 mμ for R = OMe (5×10^{-4}M-solutions in chloroform); this absorption is clearly due to the simple molecule. For *p-NN*-dimethyltricyanovinylaniline, however, the visible band (445 mμ) decreased with decreasing concentration in very dilute solutions (5×10^{-4} to 5×10^{-6}M in chloroform) whilst a band at 370 mμ simultaneously increased. An isosbestic point occurred at 403 mμ.

The anomalous deep colour of *p-NN*-dimethyltricyanovinylaniline and of the series of *N*-(2-alkoxycarbonyl-1,2-dicyanovinyl)-*N′N′*-dialkyl-*p*-phenylenediamines may therefore be attributed to some form of self-π-complexing arising from the particular molecular structure. The complex is destroyed at very high dilutions, with liberation of the simple molecules which absorb in the expected ultraviolet region.

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[7] Bellamy and Hallam, *Trans. Faraday Soc.*, 1959, **55**, 220; Bellamy and Rogasch, *J.*, 1960, 2218.
[8] Felton and Orr, *J.*, 1955, 2170.