90. *The Infra-red Spectra and Molecular Structure of Certain Isomeric Diazocyanides.*

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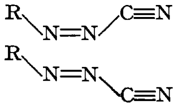
An investigation of the vibration spectra of certain isomeric diazocyanides of the Hantzsch type proves conclusively that these isomers cannot be related as cyanide and *iso*cyanide but are both cyanides.

THERE has been some controversy recently over the structure of Hantzsch's *syn*- and *anti*-diazocyanides. It was suggested by Hodgson and Marsden (*J.*, 1944, 395) that these



(I.)

R—N=N—CN

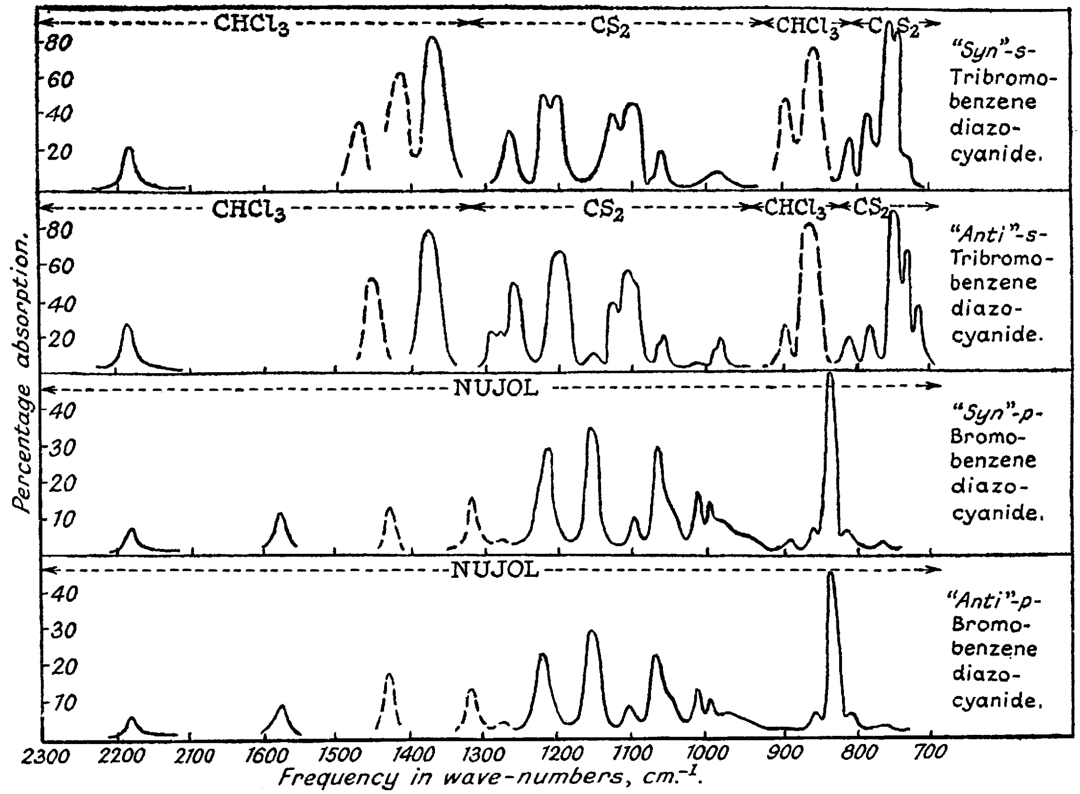
R—N=N—NC

(II.)

compounds are not *syn*- and *anti*-isomers (I), but cyanides and *iso*cyanides (II), but Le Fèvre and Vine (*J.*, 1938, 431) maintained that studies on dipole moments confirm Hantzsch's original hypothesis. The work now described arose from a query by Dr. Le Fèvre whether infra-red spectroscopy could throw any further light on this structural problem.

EXPERIMENTAL.

The compounds examined were the two 2 : 4 : 6-tribromobenzenediazocyanides (prepared by Dr. F. B Kipping) and the two 4-bromobenzenediazocyanides (prepared by Mr. D. Anderson). The spectra of all four compounds have been investigated in the infra-red between 2 μ (5000 cm.$^{-1}$) and 15 μ (667 cm.$^{-1}$), a double-beam infra-red prism spectrometer being used (Sutherland and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 174). The tribromo-compounds were examined in solution, and the monobromo-derivatives as a paste in " Nujol ". A rock-salt prism was used as the dispersing agent over the whole range, but in addition the hands near 2200 cm.$^{-1}$ were re-examined on a Hilger D88 spectrometer, a lithium fluoride prism being used to get greater precision in the determination of the position of a critical band which lies in this region. The exact position was determined by comparison with a band due to gaseous carbon disulphide which lies at 2184 cm.$^{-1}$ (Sanderson, *Physical Rev.*, 1935, **50**, 209). The spectra are given in the figure. The solvents were chloroform and carbon disulphide, an approximately 10% solution being used in each case. These solvents have absorption bands in the infra-red which interfere slightly with the determination of parts of the spectrum but not in a critical region. A few bands, the intensities of which are less certain on account of this interference, have been indicated by broken lines. Similarly, in the case of the spectra taken in Nujol, the bands between 1250 and 1450 cm.$^{-1}$ are less certain because of the characteristic hydrocarbon bands due to Nujol at 1450 and 1370 cm.$^{-1}$.



Infra-red absorption spectra of the stable (" anti ") and unstable (" syn ") forms of 2 : 4 : 6-*tribromo- and* 4-*bromo-benzenediazocyanides. The tribromo-compounds were in solution* (10% *in* $CHCl_3$ *or* 7% *in* CS_2 *in the regions indicated) ; the monobromo-compounds were in a Nujol paste.*

DISCUSSION.*

It has been shown by several workers that cyanides can be very readily distinguished from the corresponding *iso*cyanides by their vibration spectra. For instance, Gordy and Williams (*J. Chem. Physics*, 1936, **4**, 85) examined methyl, ethyl, butyl, and phenyl cyanides and the

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* The different types of CN frequency are indicated by the symbols –CN (cyanide) and –NC (*iso*cyanide). Where it is not possible to distinguish between the two the symbol CN is used.

corresponding *iso*cyanides in the infra-red between 2·9 μ (3450 cm.$^{-1}$) and 5·0 μ (2000 cm.$^{-1}$) in order to study the variation in the position of the absorption frequency corresponding to the CN stretching vibration. Their results are summarised in Table I, where we have also given the earlier Raman data due to Dadieu and Kohlrausch (*Wien. Ber.*, 1930, **139**, 165), Bhagavantam (*Indian J. Physics*, 1930, **5**, 48), and Petrikaln and Hochberg (*Z. physikal. Chem.*, 1930, **8**, *B*, 440). It was Dadieu and Kohlrausch (*loc. cit.*) who first pointed out that the CN frequency differed by about 100 cm.$^{-1}$ in going from a cyanide to the corresponding *iso*cyanide. Table I shows that this was amply confirmed by Gordy and Williams. The latter workers, however, remarked another important difference between the CN frequency in such isomers. It is that the $^-$NC absorption frequency in the *iso*cyanides is almost exactly twice as intense in absorption as the $^-$CN frequency in the cyanides.

TABLE I

CN *Frequencies in cyanides and* iso*cyanides.*

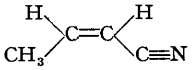
	Infra-red data, in cm.$^{-1}$.	Δν.	Raman data, in cm.$^{-1}$.	Δν.
Methyl cyanide	2283	100	2250	89
,, *iso*cyanide	2183		2161	
Ethyl cyanide	2257	97	2246	100
,, *iso*cyanide	2160		2146	
Butyl cyanide	2247	96	—	—
,, *iso*cyanide	2151		—	
Phenyl cyanide	2232	109	2232	—
,, *iso*cyanide	2123		—	

If, therefore, the pairs of isomers we examined were related as cyanides and *iso*cyanides, we should expect the CN frequency to differ in value by about 100 cm.$^{-1}$ and in intensity by a factor of 2 between the members of each pair. Instead, we find there is no difference either in position or in intensity between the CN frequency in the isomers. The exact values observed by us were as follows

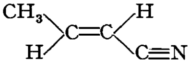
2 : 4 : 6-Tribromo- (stable derivative) 2185 4-Bromo- (stable derivative) 2185
2 : 4 : 6-Tribromo- (unstable derivative) 2187 4-Bromo- (unstable derivative) 2185

These values are correct to $\pm$ 5 cm.$^{-1}$. *This proves conclusively that these compounds are not structural isomers of the cyanide–*iso*cyanide type.* It remains to be decided whether the spectroscopic results allow one to make further deductions on their structure.

The vibration spectra of a few *cis-* and *trans*-isomers containing a CN bond have been determined. De Hemptinne and Wouters (*Ann. Soc. Bruxelles*, 1933, **53**, *B*, 215) examined the Raman spectra of *cis-* and *trans*-crotononitrile, (III) and (IV). They found the CN frequency to have the value 2235 cm.$^{-1}$ in the *trans-* and 2226 cm.$^{-1}$ in the *cis*-form, *i.e.*, a difference of less than 10 cm.$^{-1}$. The same two compounds were examined later by Reitz and Sabbathy (*Monatsh.*, 1938, **71**, 131) in what appears to be a more careful investigation. They obtained values for the CN frequency of 2217 cm.$^{-1}$ and 2220 cm.$^{-1}$, respectively, in the *cis-* and *trans*-forms, *i.e.*, a difference of only 3 cm.$^{-1}$. We may therefore conclude from the fact that each pair of our " diazocyanides " gives the CN frequency in the same position to within 10 cm.$^{-1}$, that this is strong evidence that each pair consists of a *cis-* and a *trans*-form of either a cyanide or an *iso*cyanide.



(III.)



(IV.)

The question whether the compounds are all cyanides or all *iso*cyanides is harder to decide. It will be noticed that the CN frequency in the " diazocyanides " (2185 cm.$^{-1}$) occupies an intermediate position between the $^-$CN frequency of the cyanides and the $^-$NC frequency of the *iso*cyanides in Table I, the former ranging between 2283 and 2232 cm.$^{-1}$ while the latter vary between 2183 and 2123 cm.$^{-1}$. If, then, the " diazocyanides " are cyanides, there must be some reason for the abnormally low value of their $^-$CN frequency, while if they are *iso*cyanides an explanation must be found for the increase in the $^-$NC frequency.

Let us first examine the causes of the variations in the $^-$CN frequency of the cyanides, summarised in Table II. This frequency decreases steadily in going from methyl cyanide

TABLE II.

Variations in the –CN *Frequency in Cyanides.*

(1) "Mass" effect.

	cm.$^{-1}$.
$CH_3 \cdot CN$	2283
$C_3H_5 \cdot CN$	2257
$C_3H_7 \cdot CN$	2247
$C_4H_9 \cdot CN$	2245
$C_5H_{11} \cdot CN$	2241

(2) Conjugation effect.

	cm.$^{-1}$.	$\Delta\nu$.
$Ph \cdot CH_2 \cdot CN$	2273	41
$Ph \cdot CN$	2232	
$CH_3 \cdot CH_2 \cdot CN$	2257	35 mean
$CH_2(CN) \cdot CH_2 \cdot CN$	2254	
$CH_2{:}CH \cdot CN$	2224	
$CH_2{:}CMe \cdot CN$	2224	
cis-$CH_3 \cdot CH{:}CH \cdot CN$	2217	
trans-$CH_3 \cdot CH{:}CH \cdot CN$	2220	
$CMe_2{:}CH \cdot CN$	2216	

(2283 cm.$^{-1}$) to amyl cyanide (2241 cm.$^{-1}$). This is partially a mass effect and we may reasonably assume that, on this account in the large diazocyanides under discussion here, the –CN frequency should be at the lower end of its range, *i.e.*, near 2250 cm.$^{-1}$. There is next the effect of conjugation on the –CN frequency, which is illustrated by section (2) of Table II. It will be observed that in analogous molecules conjugation of the $C\equiv N$ bond to a $C=C$ bond causes a lowering of the –CN frequency by 35—40 cm.$^{-1}$. In the diazocyanides the $C\equiv N$ bond will be conjugated to an $N=N$ bond. Unfortunately, no spectroscopic data exist on the effect of this type of conjugation on the CN frequency but it would be expected to be very similar to conjugation with a $C=C$ bond. On these grounds we may expect to find the –CN frequency abnormally low in diazocyanides for two independent reasons, and quantitatively the effects are of the right order to make the –CN frequency in diazocyanides about 2200 cm.$^{-1}$ or even slightly lower.

Let us next consider variations in the –NC frequency in the *iso*cyanides (Table III). The same "mass" effect is observed as in the cyanides and so on this account one would expect the –NC frequency in a diazo*iso*cyanide of the size we are considering to lie around 2150 cm.$^{-1}$. Unfortunately, no analogues have been examined for the conjugation effect, but the fact that it must exist is clear from the comparison of the value of the –NC frequency in butyl and phenyl *iso*cyanide in section (*b*) of Table III. On the same grounds then that we predicted a value of about 2200 cm.$^{-1}$ for the –CN frequency in a large conjugated diazocyanide, we should predict a value of about 2100 cm.$^{-1}$ for the –NC frequency in a similar diazo*iso*cyanide. The observed value of 2185 cm.$^{-1}$ in the four compounds examined by us is therefore strong evidence that these compounds are all diazocyanides and not diazo*iso*cyanides.

TABLE III.

Variations in the –NC *frequency in* iso*cyanides.*

(*a*) "Mass" effect.

	cm.$^{-1}$.
$CH_3 \cdot NC$	2183
$C_2H_5 \cdot NC$	2160
$C_3H_7 \cdot NC$	2151

(*b*) Conjugation effect.

	cm.$^{-1}$.	$\Delta\nu$.
$C_3H_7 \cdot NC$	2151	28
$Ph \cdot NC$	2123	

The discussion of the other evidence in favour of regarding these compounds as *syn-* and *anti*-diazocyanides is given in the preceding paper by Anderson, Le Fèvre, and Savage. These authors have also examined the infra-red spectra of *syn-* and *anti-p*-chloro-, -*p*-bromo-, -*p*-nitro-, and -2 : 4 : 6-tribromo-benzenediazocyanides and two of the diphenyl-4 : 4′-bisdiazocyanides. Their results confirm our observations on the *p*-bromo-compounds. Furthermore they find the CN frequency to be in exactly the same position (2185 cm.$^{-1}$) in all their other diazocyanides. The spectroscopic evidence against the *iso*cyanide theory can therefore be regarded as overwhelming.

We wish to express our thanks to Dr. R. J. W. Le Fèvre for drawing our attention to this problem and to Dr. F. B. Kipping for preparing the 2 : 4 : 6-tribromobenzenediazocyanides.

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