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INFRA-RED INTENSITY MEASUREMENTS ON DIAZOCOMPOUNDS

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Abstract—Integrated intensities and frequencies are given for the diazo and carbonyl bands of a few aromatic diazohydrocarbons and *p*-substituted diazoacetophenones. The results, compared with previous related infra-red and photochemical data, are discussed in terms of the relevant resonance structure in the different cases. Tentative arguments are given for a possible assignment of the -CNN grouping symmetrical stretching mode, apparently strongly coupled to the carbon skeletal of the molecule.

The spectroscopical and photochemical study of diazocompounds has recently been developed. In the case of diazomethane[1] the vibrational spectra have been well investigated and interpreted but this investigation for diazohydrocarbons and diazoketones is limited to the stretching frequencies of NN and CO groupings[2] and to the study of possible interactions with solvent medium.[3] The electronic spectra appear to have been examined[4] only at an introductory level, mainly in connexion with photochemical measurements, which on the other hand have given interesting information concerning structural influences on the quantum yield of the photolysis and the reactivity of the carbene fragments produced in the primary photolytic act, both in ordinary conditions[5] and in a matrix.[6] In connexion with spectroscopic–photochemical and electrochemical[7] investigation on diazocompounds, we have given some results of frequency and intensity measurements on the NN and CO stretching bands for a few simple diazohydrocarbons and for *p*-substituted diazoacetophenones; a vibrational study for a few parent molecules of this group, particularly diazocyclopentadiene and diazoacetone, is in progress.

EXPERIMENTAL

A Perkin-Elmer Model 112 spectrometer with CaF_2 optics was used throughout; the NaCl cells had a thickness of 0·121 and 1·000 mm. The data in Table 1 are for CCl_4 soln unless otherwise noted, those in Table 2 for CCl_4 soln in the case of NN and ω_3 bands, for C_2Cl_4 soln in the case of CO band; CCl_4 and C_2Cl_4 were purified by reflux over P_2O_5 and K_2CO_3 respectively, and distillation. The frequency values for the 4·8 μ, range now obtained are on an average 15 cm^{-1} higher than those reported by Yates and Shapiro[2a], the difference being due to better experimental conditions with a

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[1] B. L. Crawford, W. H. Fletcher and D. A. Ramsay, *J. Chem. Phys.* **19**, 406 (1951); W. H. Fletcher and T. P. Garrett, *Ibid.* **25**, 50 (1956); J. M. Mills and H. W. Thompson, *Trans. Faraday Soc.* **50**, 1270 (1954).

[2a] P. Yates and L. B. Shapiro, *J. Amer. Chem. Soc.* 79, 5756 (1957); [b] F. Fahr, *Liebigs Ann.* **617**, 11 (1958); [c] H. N. Beck, *Diss. Abstr.* **18**, 1250 (1958).

[3a] F. Fahr, *Chem. Ber.* **92**, 398 (1959); [b] F. A. Miller, *J. Amer. Chem. Soc.* **79**, 5974 (1957).

[4] A. J. Ultée and J. B. J. Soons, *Rec. Trav. Chim.* **71**, 565 (1952); G. Kortum, *Z. Phys. Chem.* **50**, 379 (1941).

[5] W. Kirmse, L. Horner and H. Hoffmann, *Liebigs Ann.* **614**, 19 (1958); W. Kirmse and L. Horner, *Ibid.* **625**, 34 (1959).

[6] G. Pimentel, D. E. Milligan and T. D. Goldfarb, *J. Chem. Phys.* **29**, 1405 (1958); *J. Amer. Chem. Soc.* **82**, 1865 (1960); G. W. Robinson and M. McCarty, Jr., *Ibid.* **82**, 1859 (1960); W. B. De More and N. Davidson, *Ibid.* **81**, 5869 (1959).

[7] A. Foffani, L. Salvagnini and C. Pecile, *Ann. Chim. Ital.* **49**, 1677 (1959).

more efficient standardization through the 4·6 μ CO band. The data here reported are, therefore, more accurate than the previous ones, with an estimated accuracy of ± 2 cm^{-1}.

The integrated intensities, in units mole^{-1} litre cm^{-2}, were measured with the Wilson–Wells method as previously described;[8] the estimated spectral slit-width was 5·4–4·1 cm^{-1}. The integration was extended over an interval of about 100 cm^{-1}, the overlapping with neighbouring bands often being negligible and, when necessary, being corrected for graphically. The concentration of the solutions was in the range 5·10^{-2}–3·10^{-3} moles/litre for the NN band, 8·10^{-2}–6·10^{-2} moles/litre for CO band. At least four independent intensity determinations were performed on any band of any single compound. All compounds were carefully purified during preparation.[9]

RESULTS AND DISCUSSION

Tables 1 and 2 give frequency, integrated intensity and half-width values for the NN and CO stretching bands of the compounds examined. As only limited information is available concerning the assignment of bands in the spectra of diazocompounds other than diazomethane, it was of interest to examine first the possible position of the (pseudo)-symmetrical stretching mode of the -CNN triatomic group which characterizes these compounds. In the following footnote* the average frequency ranges are given for other organic molecules with triatomic group vibrationally correlated to diazocompounds, implying a (pseudo)-asymmetrical stretching frequency located in the range characteristic of triple bonds or of cumulated double bonds. In the case of diazomethane this is correctly assigned at 852 cm^{-1} [1] but for other aliphatic diazohydrocarbons there is no indication, while the spectra for aromatic diazohydrocarbons do not indicate a reliable position.

On the other hand, diazoketones[2] and diazoesters show a strong band at 1335–1410 cm^{-1}, not observed in diazohydrocarbons with the exception of diazocyclopentadiene[12a] which shows a strong band at about 1300 cm^{-1} not present in cyclopentadiene.[12b] Such a band can not correspond to a CH deformation mode for monosubstituted diazoketones, as it is also observed in the disubstituted compounds. In addition the carbonyl skeletal vibration ($\nu_4 \sim 1225$ cm^{-1} for acetone[13]) and the ω_3 aromatic ring mode should be assigned to a lower frequency interval, falling for example around 1255 cm^{-1} for acetophenones and most probably, around 1225 cm^{-1} for diazoacetophenones, with shape and intensity clearly different from those of the band being discussed (see below). These arguments seem to support the possible

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* RN_3, $RCON_3$, 1340–1180 cm^{-1}; RNCO, ~1350 cm^{-1}; RNCS, RSCN, ~680 cm^{-1}; allene, 1070 cm^{-1}; CH_2CO, 1124 cm^{-1}.[10] Additional examples may be drawn from data available also for triatomic molecules and inorganic anions: CN_2^{2-}, 1234 cm^{-1}; SCO, 859 cm^{-1}; NCS^-, 750 cm^{-1}; NCO^-, 1300 cm^{-1}; N_3^-, 1344 cm^{-1} and so forth.[11]

[8] A. Foffani, C. Pecile and F. Pietra, *Nuovo Cimento* **13**, 213 (1959); D. A. Ramsay, *J. Amer. Chem. Soc.* **74**, 72 (1952).

[9] $C_6H_5CHN_2$: A. Hantzsch and M. Lehmann, *Chem. Ber.* **35**, 897 (1902); $(C_6H_5)_2CN_2$: L. I. Smith and K. L. Howard, *Organic Syntheses* Coll. Vol. III, p. 351 (1955); $C_6H_5COC(C_6H_5)N_2$: C. D. Nenitzescu and E. Solomonica, *Ibid.* Coll. Vol. II, p. 496 (1943); CH_3COCHN_2: F. Arndt and J. Amende *Chem. Ber.* **61**, 1122 (1928); Diazoacetophenones: A. L. Wilds and A. L. Meader, *J. Org. Chem.* **13**, 763 (1948); W. Bradely and G. Schwarzenbach, *J. Chem. Soc.* 2904 (1928); L. Canonica, *Gazz. Chim. Ital.* **80**, 412 (1950); Diazocyclopentadiene: W. von E. Doering and C. H. De Puy, *J. Amer. Chem. Soc.* **75**, 5955 (1953).

[10] Yu. N. Sheinker and Ya. K. Syrkin, *Izv. Akad. Nauk SSSR, S.F.* **14**, 478 (1950); N. S. Ham and J. B. Willis, *Spectrochim. Acta* **16**, 279 (1960); J. Lecomte, *Handbuch der Physik* Band XXVI, pp. 595, 499, 409. Springer, Berlin (1958); J. Goubeau and J. Reyhing, *Z. Anorg. Chem.* **294**, 96 (1958).

[11] S. K. Deb and A. D. Yoffe, *Trans. Faraday Soc.* **55**, 106 (1959); J. Lecomte, *loc. cit.* pp. 747, 748; T. C. Waddington, *J. Chem. Soc.* 2500 (1959); P. Gray and T. C. Waddington, *Trans. Faraday Soc.* **53**, 901 (1957).

[12a] W. von E. Doering and C. H. De Puy, *loc. cit.*; [b] American Petroleum Institute research Project 44, National Bureau of Standards (U.S.A.) Catalog of Infra-red Spectral Data, serial N. 458; J. Lecomte, *Bull. Soc. Chim.* **13**, 415 (1946).

[13] S. A. Francis, *J. Chem. Phys.* **19**, 942 (1951).

assignment of the band 1300–1400 cm^{-1} to the symmetrical stretching mode of $>$CNN grouping, strongly raised in its frequency for compounds showing a high degree of conjugation implying a relevant electron shift from diazogroup and an increasing degree of coupling of the triatomic $>$CNN grouping to the skeletal of the molecule, giving this symmetrical mode a higher character of skeletal mode. In order to clarify this problem, a structural study is clearly necessary.

TABLE 1. DIAZOHYDROCARBONS AND DIAZOKETONES

Compounds	ν_{NN} cm^{-1}	$A_{NN} \times 10^{-4}$	$\Delta\nu_{1/2}$	ν_{CO} cm^{-1}	$A_{CO} \times 10^{-4}$	$\Delta\nu_{1/2}$
CH_2N_2	2088[a]					
$CHC_6H_5N_2$	2062	4·2				
$CC_6H_{12}N_2$	2042	7·3_5				
Diazocyclopentadiene	2089	5·8				
CH_3COCHN_2	2107[b]	3·7_3[b]		1659	2·8	15
$C_6H_5COCHN_2$	2108	5·8_5	14	1633	1·8	11
$C_6H_5COC(C_6H_5)N_2$	2072	5·4_6	14	1636	2·7	14
$C_2H_5OOCCHN_2$	2117[c]			1695[c]		

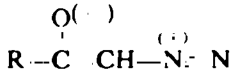
[a] Ethereal soln.; [b] Corrected for the contribution of a weaker band at 2090 cm^{-1}; [c] from Yates[14]; ν_{NN} corrected by −16 cm^{-1} (see Experimental).

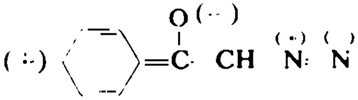
TABLE 2. DIAZOACETOPHENONES[a]

X–C_6H_4–CO–R	R = CHN_2							R = CH_3[b]		
	ν_{NN} cm^{-1}	$A_{NN} \times 10^{-4}$	$\Delta\nu_{1/2}$	ν_{CO} cm^{-1}	$A_{CO} \times 10^{-4}$	$\Delta\nu_{1/2}$	ω_3 cm^{-1}	ν_{CO} cm^{-1}	$A_{CO} \times 10^{-4}$	ω_3[d] cm^{-1}
X = p-OCH_3	2105	6·0	11	1631	2·4	12	1227	1682	2·1_4[c]	1258 l
p-CH_3	2108	5·4	12	1634			1228	1687	2·4_4	1265 s
p-H	2108	5·8_4	14	1634	1·8_5	10	1223	1691	2·2_6	1260 s
p-Cl	2109	4·6_5	13	1632	2·0	13	1218	1692	2·2_5	1259 l
p-NO_2	2112	5·4_7	14	1642	1·6_5	13	1215	1700	1·9_4	1238 s

[a] Data for NN and ω_3 band as CCl_4 soln. for CO band as C_2Cl_4 soln. [b] see[14]. [c] as $CHCl_3$ soln[14]. [d] l → liq s → solid [14]

In this connexion it may be mentioned that similar frequency shifts of the asymmetrical vibration[2] have been observed. In the case of aliphatic diazohydrocarbons there is a gradual frequency decrease of this band by increasing the number of substituents at carbon, independent in a first instance of the type of substituent. The aromatic diazohydrocarbons behave similarly, apparently through some kind of compensation of the effects of the two structures due to diazogroup–aromatic ring conjugation with either positive or negative charge at the *para* carbon atom. This is also supported by the high frequency value of the $>$CNN asymmetrical stretching mode for diazocyclopentadiene (2089 cm^{-1}, to be compared with the corresponding average figure 2040 cm^{-1} for disubstituted aromatic diazohydrocarbons), where such a competitive effect of conjugated structures is not operative, there being only the strong mesomeric electron donating effect of diazogroup towards the cyclopentadiene ring, apparently owing to the prevalence of a structure of the type $\overset{(-)}{C_5H_4}-\overset{(+)}{N}\equiv N$. Presumably this effect might cause for this molecule, as distinct from aromatic diazohydrocarbons,[5] a relevant lowering of the quantum yield for the photolysis.

In aliphatic α-diazocarbonyl compounds containing the same number of substituents, a single α-carbonyl causes a frequency increase of the ν·CNN asymmetrical stretching mode by an average of 40 cm^{-1}, through the intervention of a structure of type:  $R{-}\overset{O(-)}{C}{=}CH{-}\overset{(+)}{N}{\equiv}N$ involving diazogroup–carbonyl conjugation; the effect is further enhanced by addition of a second α-carbonyl group. It is of interest to note, that in diazoacetone and diazoacetophenone (see Table 1), although aromatic substitution does not appreciably effect the ν·CNN asymmetrical stretching mode frequency, it lowers the corresponding carbonyl stretching frequency by 25 cm^{-1}, a lowering almost equal to the 24 cm^{-1} observed in acetone and acetophenone. This is due to the intervention of the normal carbonyl phenyl conjugative structure, which in this case is of the type:



involving on diazo-band a partial compensation of the diazo carbonilic conjugative effect, while enhancing this very effect on the carbonyl stretching frequency, with an additional contribution for an amount almost equal to the one observed for other conjugated carbonyl compounds. Similarly the quantum yield of the photolysis[6] is lowered by about 0·2 units on going from diazobutanone to diazoacetophenone.

The parallelism ketones-diazoketones as to aryl-substitution is also reflected on the substituent effects to aromatic ring on the carbonyl stretching frequency, which are in the same direction and of the same order of magnitude for the frequency as well as for the intensity (see Table 2), although the effect on the intensity is very small.* Other couples which may be compared are for example ethyl acetate-ethyl benzoate and phenyl acetate-phenyl benzoate, with carbonyl frequency lowerings 22 and 25 cm^{-1} respectively and similar *p*-substitution effects on frequency and intensity.[14a,b] In this connexion it may be noted that the quantum yield for the photolysis of diazoacetophenone shows[5] a tendency to decrease for every type of *ortho*- or *para*-substitution, an effect not yet understood.

As to the absolute values of the intensities it may be observed instead that for diazoacetone and diazoacetophenone the aryl-substitution causes a strong intensity decrease for 1 mole^{-1} litre cm^{-2}, compared[14a,b] with an increase of about 0·5 units for the couple acetone acetophenone, while for the couples ethyl acetate–ethyl benzoate and phenyl acetate–phenyl benzoate there are only small variations, which are within the limits of experimental error. The apparently anomalous effect on the intensity of carbonyl band is probably due to the strong mesomeric effect of the diazo group, as is reflected in the exceptionally low value of the carbonyl frequency for the compounds†

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* Table 2 reports also the frequency of the band at 1215–1230 cm^{-1} for the *p*-substituted diazoacetophenones, compared with the one at 1240–1265 cm^{-1} for the acetophenones; as before mentioned, the intensity and shape of the two bands, their position and the parallel trend of the substituent effect strongly support their common assignment to the ω_3 aromatic ring in-plane skeletal mode, well known for being substituent sensitive and which in the present case perhaps is also partaking, at least partially, the character of the carbonylic skeletal mode (ν_4 = 1225 cm^{-1} for acetone) falling in the same range.

† For example: ν_{CO} (acetone)–ν_{CO}(diazoacetone) = 56 cm^{-1}; ν_{CO}(acetophenone)–ν_{CO}(diazoacetophenone) = 57 cm^{-1}; ν_{CO}(ethyl acetate)–ν_{CO}(ethyl diazoacetate) = 47 cm^{-1}.

[14a] H. W. Thompson and D. A. Jameson, *Spectrochim. Acta* **13**, 236 (1958); [b] *Ibid.* **9**, 208 (1957); [c] R. N. Jones, *Canad. J. Chem.* **35**, 504 (1957); [d] B. P. Susz and P. Chalandon, *Helv. Chim. Acta* **41**, 1338 (1958).

and in the particularly high value of the $>$·CNN asymmetrical stretching mode for diazocyclopentadiene. Trichloro and trifluoro-diazoacetone[2c,15] are unusual due to the superposition of the strong inductive effect of the –$CHCl_3$ grouping, the carbonyl band shift being 80 cm^{-1} for CCl_3COCH_3 and CCl_3COCHN_2 and 112 cm^{-1} for the trifluoro-derivatives.

As to the intensity of the $>$·CNN grouping asymmetrical stretching mode in diazohydrocarbons and diazocarbonyl compounds, the situation appears to be more involved and difficult to interpret due to the limited data presently available. There seems to be a rough parallelism with the characteristic structural effects on the frequency, with a strong influence of the substitution at carbon atom on the degree of coupling within the $>$·CNN grouping: the intensity increases strongly on going from phenyl- to diphenyl-diazomethane but the behaviour of diazocarbonyl compounds is less clear, presumably owing to the competitive action of carbonyl-phenyl conjugation, difficult to evaluate in its effect on the diazoband intensity.

[15] L. J. Bellamy and R. L. Williams, *J. Chem. Soc.* 4304 (1957).