

**780.** *Characteristic Infrared Absorption Frequencies in the cis-trans Isomers of Dimeric Nitroso-alkanes.*

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From tables presented of the characteristic infrared absorption frequencies of *trans* and *cis* dimers of nitroso-alkanes it appears that unknown dimers could be reliably assigned the *cis* or *trans* structure on the basis of such spectra.

BELLAMY<sup>1</sup> noted that different workers have assigned the N-O stretching frequency in C-nitroso-compounds to the range of either 1310—1420 or 1640—1650 cm.<sup>-1</sup>. More recent measurements<sup>2-6</sup> of the infrared absorption spectra of C-nitroso-compounds have indicated that the N-O stretching frequency in C-nitroso-monomers differs from that in the C-nitroso-dimers: in the monomers the range is 1500—1650 cm.<sup>-1</sup>. The C-nitroso-dimers exhibit geometrical isomerism about the N-N bond which has considerable double-bond

<sup>1</sup> Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London, 1954, p. 254.

<sup>2</sup> Tarte, *Bull. Soc. chim. belges*, 1954, **63**, 525.

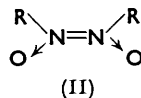
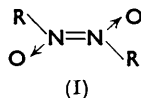
<sup>3</sup> Glusker and Thompson, *Spectrochim. Acta*, 1954, **6**, 434.

<sup>4</sup> Nakamoto and Rundle, *J. Amer. Chem. Soc.*, 1956, **78**, 1113.

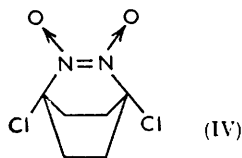
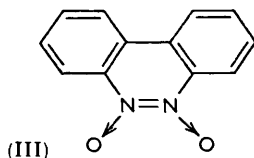
<sup>5</sup> Müller and Metzger, *Chem. Ber.*, 1954, **87**, 1282, 1449; 1955, **88**, 165, 1891.

<sup>6</sup> Lüttke, *Angew. Chem.*, 1956, **68**, 417. *Z. Elektrochem.*, 1957, **61**, 302.

character; the predominant electronic structures are indicated in (I) and (II). Characteristic frequencies for the *cis* and *trans* dimers must be considered separately and, once established, can be used to distinguish the isomers in cases of doubt.



Most *C*-nitroso-dimers as prepared by older methods (cf. Sidgwick <sup>7</sup>) are *trans* and some have N-O stretching frequencies <sup>2,6</sup> corresponding to strong infrared absorption bands in the region 1160—1300  $\text{cm}^{-1}$ . Dimeric nitrosobenzene exists in the *cis* form <sup>6</sup> and has a strong double absorption band at 1380—1420  $\text{cm}^{-1}$ . Benzocinnoline *NN'*-dioxide (III) and *cis*-1 : 4-dichloro-1 : 4-dinitrosocyclohexane (IV), which are limited for steric reasons



to internal dimerization of the nitroso-groups in the *cis* configuration, exhibit <sup>6</sup> a similar double band. Recent preparative methods for dimeric nitroso-alkanes <sup>8</sup> afford new compounds of each configuration for substantiating and extending the characteristic frequency assignments quoted above.

#### EXPERIMENTAL

*cis*-Dimeric nitroso-alkanes were prepared by Gowenlock and Trotman's method.<sup>8</sup> *trans* Dimers were prepared by shaking the corresponding *cis* dimer with carbon tetrachloride until the almost insoluble *cis* dimer had been completely transformed to the soluble *trans* dimer. In some cases the solid *trans* dimer crystallized from such solutions on evaporation. The spectra were measured within 48 hr. of preparation and the materials stored in the dark; no evidence of oxime formation was observed in the spectra, except in that of the *trans* dimer of 2-nitrosobutane. Measurements were made with a single-beam Grubb-Parsons spectrometer with a rock-salt prism. The extinction coefficients are given by  $\epsilon = \log_{10} (I_0/I)_{\text{max.}}/cl$  with  $c$  in moles/l. and  $l$  in cm. as recommended by Jones and Sandorfy,<sup>9</sup> and are very approximate in view of the difficulties of absolute measurement especially with potassium chloride discs.

#### RESULTS AND DISCUSSION

The frequencies of the strong bands of the *trans* dimers are given in Table 1. The usual pattern in carbon tetrachloride solution contains an extremely strong band near 1215  $\text{cm}^{-1}$  and a strong band near 1145  $\text{cm}^{-1}$ . The frequencies are scarcely different in the solids, though the bands broaden slightly and the maximum extinction coefficients are consequently lower. The methyl compound is anomalous in that its strongest band is at 1290  $\text{cm}^{-1}$ : the frequencies of the *sec*-pentyl dimer are low, possibly for some steric reason. Müller and Metzger <sup>5</sup> have shown that other secondary *trans* dimers exhibit a low frequency for the band which they ascribe to the antisymmetric N-O stretching mode, their values being 1199  $\text{cm}^{-1}$  (*cyclo*-C<sub>6</sub>H<sub>11</sub>), 1198  $\text{cm}^{-1}$  (*cyclo*-C<sub>7</sub>H<sub>13</sub>), 1182  $\text{cm}^{-1}$  (*cyclo*-C<sub>8</sub>H<sub>15</sub>) 1183  $\text{cm}^{-1}$  (Pr<sup>n</sup><sub>2</sub>CH). However in *trans*-dimeric nitrosotoluene this frequency drops <sup>5</sup> to 1166  $\text{cm}^{-1}$ . The values of Table 1 for R = Me and Bu<sup>t</sup> agree well with those of Tarte <sup>2</sup> and Jander and Haszeldine.<sup>10</sup> In contrast, the *cis* dimers do not have bands with  $\epsilon$  above

<sup>7</sup> Sidgwick, "Organic Chemistry of Nitrogen," Oxford Univ. Press, 1937, p. 204.

<sup>8</sup> Gowenlock and Trotman, *J.*, 1955, 4190; 1956, 1670.

<sup>9</sup> Jones and Sandorfy, "Chemical Applications of Spectroscopy" (Ed. W. West), Interscience, New York, 1956, p. 271.

<sup>10</sup> Jander and Haszeldine, *J.*, 1954, 912.

80 in the 1215  $\text{cm}^{-1}$  region and the absorption quoted must be considered characteristic of the *trans* dimers. The *trans*-dimer (I) skeleton has essentially  $C_{2h}$  symmetry and two  $B_u$  class skeletal frequencies are expected to lie above 900  $\text{cm}^{-1}$  and absorb strongly in the infrared region; they may be regarded as due essentially to the antisymmetric N-O and C-N stretching vibrations. The N-O bonds may have partial double-bond character and are strongly polar; the higher frequency and more intense bands of column (i) are

TABLE 1. *Infrared absorption of trans dimers (RNO)<sub>2</sub>.*

R	CCl <sub>4</sub> solution				Solid in KBr or KCl			
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
	$\text{cm}^{-1}$	$\epsilon$	$\text{cm}^{-1}$	$\epsilon$	$\text{cm}^{-1}$	$\epsilon$	$\text{cm}^{-1}$	$\epsilon$
Me .....	1290	1500	1129	150	1286	300	1134	100
Et .....	1222	600	1143	150				
Pr <sup>a</sup> .....	1210	600	1140	150				
			1117	250				
Pr <sup>l</sup> .....	1212	500	1140	150				
Bu <sup>a</sup> .....	1211	700	1148	200	1212	300	1144	100
			1116	250			1120	20
Bu <sup>l</sup> .....	1218	600	1147	150	1215	250	1144	150
Bu <sup>s</sup> .....					1200	vs †	1172	m †
							1118	m †
							1093	m †
Bu <sup>t</sup> .....		*			1262	400	1181	200
					1233	250		
<i>sec</i> -C <sub>5</sub> H <sub>11</sub> ...	1193	900	1096	100	1191	600	1100	100

\* Dissociates to monomer.

† Liquid of uncertain purity.

The full spectra of the solids in Tables 1 and 2 have been offered to the Documentation of Molecular Spectroscopy punched-card collection.

TABLE 2. *Infrared absorption of cis dimers (RNO)<sub>2</sub> in KCl or KBr.*

R	(i)		(ii)		(iii)		(iv)		(v)	
	$\text{cm}^{-1}$	$\epsilon$	$\text{cm}^{-1}$	$\epsilon$	$\text{cm}^{-1}$	$\epsilon$	$\text{cm}^{-1}$	$\epsilon$	$\text{cm}^{-1}$	$\epsilon$
Me .....	1387	300	1341	60	—	—	1107	40	1061	30
	(dbl. ?)								1017	200
Et .....	1426	80	1323	30	1290	40	1078	50	1043	90
	1370	90								
Pr <sup>a</sup> .....	1431	100	1332	60	1302	50	1082	50	1056	40
	1406	150							1044	80
	1381	70								
Pr <sup>l</sup> .....	1426	80	1330	70	1300	30	1082	40	1040	90
	1408	150							(dbl.)	
	1382	80								
Bu <sup>a</sup> .....	1426	100	1336	50	1296	30	1096	70	1041	150
	1385	150								
Bu <sup>l</sup> .....	1418	40	1338	30	1304	20	1095	50	1039	80
	1382	70			1287	30				
Bu <sup>s</sup> .....	1420	80	1338	50	1296	40	1096	50	1040	100
	1384	100								
<i>sec</i> -C <sub>5</sub> H <sub>11</sub> ...	1408	150	1323	90	1306	40	1087	80	1045	40
	1377	130					(dbl.)		1031	60

likely to be mainly due to the stretching of these bonds, though doubtless some mixing with the C-N stretching, and other modes, can occur. The symmetric vibrations, including the N-N stretching, will be inactive in the infrared region and must be sought in the Raman spectra.

Table 2 indicates the strong bands above 1000  $\text{cm}^{-1}$  in the *cis* dimers measured in potassium halide discs. These have been sorted into five columns which are believed to correspond to five characteristic vibrations of the skeleton, though it is possible that some feature of the alkyl group has been included. The basic skeleton (II) has  $C_{2v}$  symmetry and both the  $A_1$  class, which includes the symmetric N-O and C-N stretching modes and the N-N stretching mode, and also the  $B_1$  class, with the antisymmetric N-O and C-N stretchings, will contain infrared-active vibrations. Column (i) includes bands from

1370 to 1440  $\text{cm}^{-1}$ , all of which are of considerable strength. This region is that in which C-H deformation vibrations normally absorb and it seems probable that these vibrations are coupled with a N-O stretching mode which also lies in this range. The *cis* dimer of nitrosomethane shows only one rather broad and very strong line in this range even though a  $-\text{CH}_3$  deformation frequency is to be expected as well as the N-O stretching frequency. Columns (ii) and (iii) indicate that two further characteristic frequencies lie near 1330 and 1295  $\text{cm}^{-1}$  but, though plausibly assigned to the second N-O stretching mode and the N-N stretching mode, there is no confirming evidence and no indication as to which is which. Again the methyl compound is anomalous in that there is no frequency between 1109 and 1341  $\text{cm}^{-1}$  to be associated with column (iii). By analogy with the *trans* compounds, the lower-frequency bands near 1085  $\text{cm}^{-1}$  [column (iv)] and 1040  $\text{cm}^{-1}$  [column (v)] are tentatively assigned to the two C-N stretching modes.

Even though the detailed interpretations suggested above may be wrong the characteristic differences in the infrared spectra may clearly be used to supplement the ultraviolet spectra <sup>8</sup> in distinguishing the isomers.

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