1097. *The Infrared Spectra of* 1,1-*Dinitro-carbanion Salts*

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1,1-Dinitro-carbanion salts show five characteristic regions of absorption in the infrared: I, ~1482; II, ~1360; III, ~1250; IV, ~1154; V, ~746 cm.$^{-1}$. Bands I and III probably correspond to the nitro asymmetrical and symmetrical stretching frequencies, band V to a nitro bending vibration, and band IV to a N–C–N stretching mode. Comparison of the spectra of potassium dinitromethane and potassium deuterodinitromethane lends evidence for these assignments. A relationship between nitro asymmetrical stretching frequencies of nitro-compounds and C–N bond-orders is suggested.

Infared spectra of 1,1-dinitro-carbanion salts have been the subject of sporadic discussion during the past decade. Brown [1] first attributed bands at 1241 and 1151 cm.$^{-1}$ in the potassium 1,1-dinitroethane spectrum to asymmetrical and symmetrical nitro stretching vibrations, respectively. Registering agreement with Brown as to their derivation, Kaplan [2] showed that the corresponding bands in fourteen additional dinitro-carbanion potassium salts fall within the ranges 1273—1240 and 1190—1150 cm.$^{-1}$ Other workers observed [3,4] that a third strong band at ~1480 cm.$^{-1}$ also seems to be common to the spectra of a number of 1,1-dinitroalkane salts as well as hydrazinium ethyl dinitroacetate and hydrazinium dinitroacethydrazide, but have not commented as to its assignment except in suggesting [3] that this region is not characteristic of N–O vibrations in an uncharged nitro-group.

In the light of the latter observations, and since there seemed to be no *a priori* basis for the Brown–Kaplan band-attributions, we undertook a comprehensive study of dinitro-carbanion infrared spectra. We now report that, based on the spectra of twenty-nine 1,1-dinitro-carbanion salts, saturated and unsaturated and containing a wide variety of additional functionality, there appear to be five regions of absorption common to, and characteristic of, this class of compounds: band I, 1516—1442; II, 1430—1333; III, 1300—1205; IV, 1220—1105; V, 764—715 cm.$^{-1}$. We also offer evidence that alternative assignments may be more reasonable for the nitro asymmetrical and symmetrical stretching modes.

RESULTS

All features of the infrared spectra as determined on pressed potassium bromide pellets are listed in Table 1. The compounds studied, which include representative members of most classes of dinitrocarbanion salts thus far reported,[5] may conveniently be divided into categories comprising potassium salts of dinitromethane and its nitro-, halogeno-, and cyano-derivatives (compounds 1—5), simple 1,1-dinitroalkanes (6—8), 3-substituted and 3,3-disubstituted 1,1-dinitropropanes (9—11 and 27, 28), 2-substituted 1,1-dinitroethanes (12—16), 1-substituted 3,3-dinitroprop-1-enes (17—19), dipotassium ααωω-tetranitroalkanes (20—22), dipotassium di-(2,2-dinitroethoxy)methane and derivatives (23—25), and a single zwitterionic salt (26).

It may be seen that many of these spectra are quite detailed in the 700—1600 cm.$^{-1}$ region. For this reason, and to facilitate intercomparisons among the large number of compounds, the chart in Figure 1 was constructed. Positions of all bands are denoted by rectangular bars whose edges mark the positions of the band-edges at half-height and whose heights on a 1-2-3 scale indicate whether the absorption is weak, medium, or strong.

In an attempt to distinguish between bands due to the dinitro-carbanion grouping and those attributable to other functionality, two approaches were used. In the case of thirteen salts (denoted by asterisks) it was possible to compare spectra with those of suitable reference compounds where the $-C(NO_2)_2^-$ grouping was replaced by $-C(NO_2)_2H$, $-C(NO_2)_2Hal$, or $-C(NO_2)_3$.

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[1] J. F. Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.
[2] L. A. Kaplan, *J. Org. Chem.*, 1964, **29**, 1638.
[3] V. I. Slovetskii, S. A. Shevelev, V. I. Erashko, A. A. Feinzil'berg, and S. S. Novikov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, 1126; 1963, 57.
[4] L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, 1958, **23**, 1340; 1960, **25**, 1471.
[5] P. Noble, F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, 1964, **61**, 19.

A number of bands common to the spectra of the salts and the reference compounds could then be eliminated with a fair degree of confidence as being attributable to other common structural features. The solid bars in Figure 1 represent such cases. In certain instances where salts and reference compounds absorbed in the same region the situation appeared less clear-cut because (*a*) intensity in the salt spectrum was substantially greater than with the reference compound,

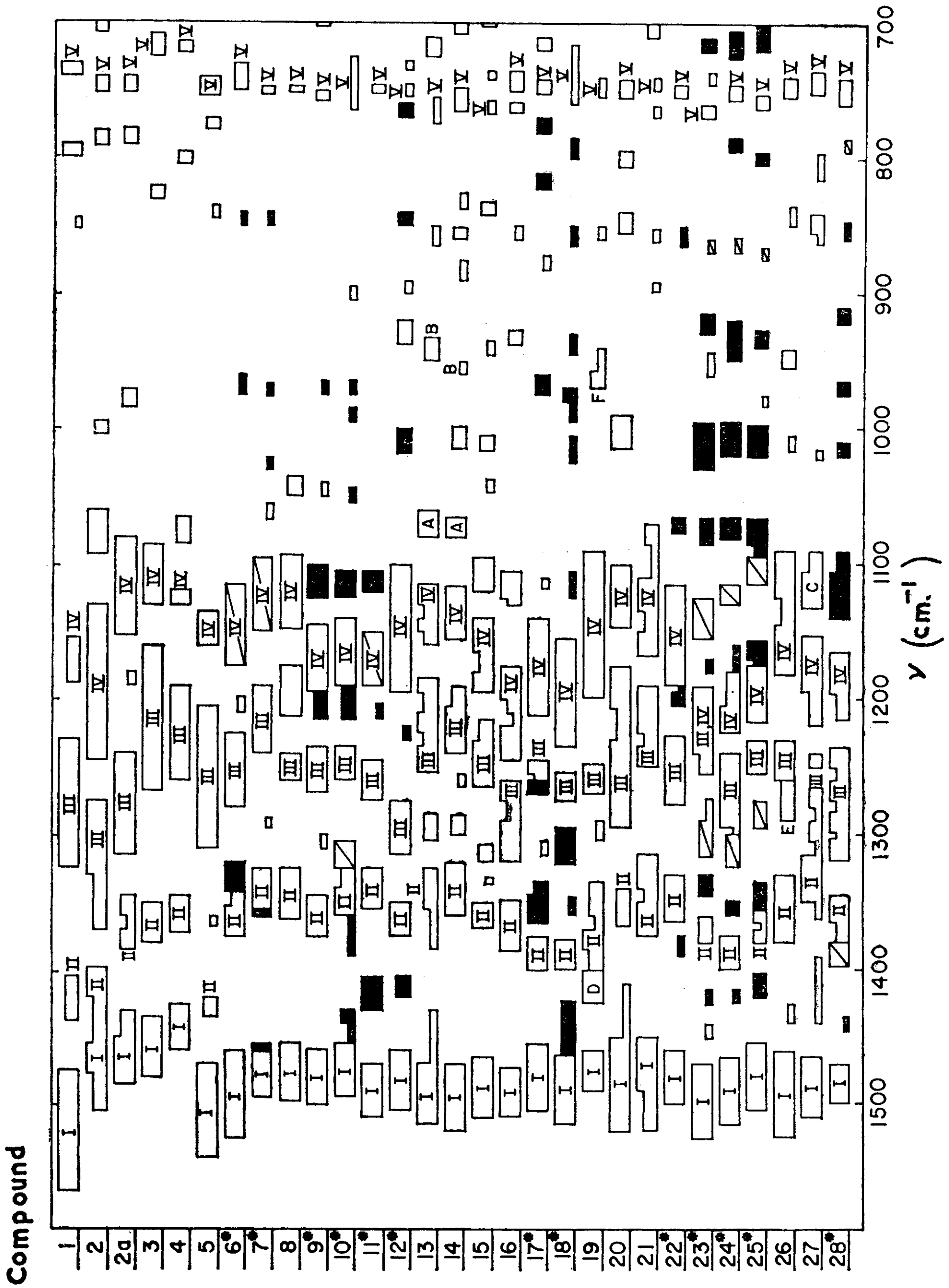

FIGURE 1. Infrared spectra of 1,1-dinitro-carbanion salts. For compounds see Table 1. For assignments of bands I—V and A—F see text

TABLE 1

Infrared spectra (cm.$^{-1}$) of 1,1-dinitro-carbanion salts *

Compound	680— 1000	1000— 1200	1200— 1300	1300— 1400	1400— 1550	Above 1550
(1) $K^{+}\,{}^{-}C(NO_2)_3$	733s 795s 874w	1177m	*1283*s, br		1424m *1516*s, br	
(2) $K^{+}\,{}^{-}C(NO_2)_2H$	694m 748m 786m	1001m 1081s	1205*s, br*	*1300s* 1363m	[1462] [1407]s [1438] [1481sh]	3140m
(2a) $K^{+}\,{}^{-}C(NO_2)_2D$	750m 781m 980m	*1135s* 1182w	*1285s*	1353m 1373m	[1465]s [1450sh]	2380w
(3) $K^{+}\,{}^{-}C(NO_2)_2Cl$	717m 827w	[1105]s [1125]	1205s, br	1360s	1452s	
(4) $K^{+}\,{}^{-}C(NO_2)_2Br$	717m 820w	1080m 1127s	*1236s, br*	1358s	*1442s*	
(5) $K^{+}\,{}^{-}C(NO_2)_2CN$	749s 773m 854w	1155s	*1265s, br*	1364w	1430m *1505s, br*	2280m
(6) $K^{+}\,{}^{-}C(NO_2)_2CH_3$	733m 849w 965w	*1158s*	1204w *1256s*	[1356]s [1335]	1495s	2960w
(7) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}CH_3$	750m 841w 970w	1022w 1062w *1128s*	[*1222*] [1205sh]s [1193sh] 1292w	[1336]s [1352sh]	[1479]s [1463sh]	2975w
(8) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	685w 750w	1042m *1123s* [*1197*]s [1185]	1245s	[1339]s [1355sh]	1479s	2950m 2870w
(9) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$	694m 752m 972w	1041w *1118s* *1171s*	1208w 1255s	1302w 1358s	1480s	2315w
(10) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2CH_3$	732w 744w 756w 902m 972m 991m	1049w 1118s *1174s*	1207m *1244s*	1317s 1341s 1380w	1439w 1475s	1734s
(11) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CONH_2$	714w 750m	1114s *1164s*	1216w *1258s*	1338s	1419m 1483m	1604w 1675s 3330w 3430w
(12) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}OH$	682m 733w 750w 761m 846m 895w 932m	1010s *1155s, br*	1223w [*1293*]s [1303sh]	1358s	1410m 1479s	2940w 3490m
(13) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}O{\cdot}CH_3$	715m 764w 854w 940m	1075s [*1128*] [*1141*]s [1155sh]	[*1240*] [1220]s [1200] 1292m	1338m 1380w	1445w 1490s	2950w
(14) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3$	702m 756m 832w 853m 880w 952w	1006m 1074s *1137s*	[*1218*]s [1208sh] 1269w 1294m	1339s	1494s	2890w 2970w
(15) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}N(CH_3)_2$	702m 740w 759w 838m 940w	1012m 1042w [1108]s [1114] [*1153*]s [1161] 1185s	[*1246*]s [1227sh]	1315m 1338w 1358m	1489s	2775w 2830w 2890w 2960w

TABLE 1 (*Continued*)

Compound	680—1000	1000—1200	1200—1300	1300—1400	1400—1550	Above 1550
(16) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}CN$	691m 745m 761m 852w 932m	*1115*s 1126w *1192s*	1208m 1226s 1269m	[1300] [1317sh] s 1333w [1372] [1350sh] s	1486s	2310w
(17) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH{:}CH{\cdot}CN$	715m 748m 778m 818m 874w 972w	1113w *1183s, br*	[1257] [1267] s	[1360] [1344sh] s 1314w 1384m	1480s	1600s 2250m 3075w
(18) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH{:}CH{\cdot}CO_2CH_3$	718w 735w 788w 852w 934w 974m 988w	1015w 1115w	*1220s, br* 1264s	*1316s* 1346w 1388s	1436m 1493s	1616s 1702m
(19) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH{:}CH{\cdot}CONH_2$	751w 852w 948w 962m	[*1168*] [1122sh] s, br	1259s 1295w	[1405] [1374]s [1349]	1470s	*1589s* 1630w 1678s 3170w 3340m
(20) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}C(NO_2)_2^{-}\ K^{+}$	751m 798m 852m	1005s 1138s *1197s*	*1262s*	1352m	[1478] [1420sh] s	
(21) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}C(NO_2)_2{-}\ K^{+}$	700m 747w 775w 859w 890w	1079m *1120s* 1155s	*1215s* 1235s	[1356] [1331] s	[1472] [1500] s	
(22) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(NO_2)_2{-}\ K^{+}$	691m 755m 856w	1070m *1157s, br*	1200m *1254s*	1347s 1481w	1481s	2940w
(23) $(K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}O]_2CH_2$	715m 737w 764m 864w 921m 952w	1014s 1075m *1144s* 1174w	[*1230*] [1250sh] s 1281w	1304m 1339m 1370m	1420w 1443w 1497s	
(24) $[K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH(CN){\cdot}O]_2CH_2$ (monohydrate)	715m 752m 791m 857w 931m	1006s 1073s 1123s 1163w 1194w	*1217s* *1276s, br*	1313m 1356m 1389s	1420w 1492s	2300w 2940w 3450w, br
(25) $[K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH(CONH_2){\cdot}O]_2CH_2$ (dihydrate)	710w 758m 800m 871w 932w	1009s 1074s *1112s* 1176s	*1209s* *1241s* 1284m	[1342] [1358]m [1373]	1416m [1486] [1471] s	1604w 1690s 2950w 3300w 3405m 3540w
(26) ${}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}NH_3^{+}$	747m 840w 952m	1005w 1116s *1166s*	[*1250*] [1270sh] s	1358s	1432w 1488s	3150s 3420s 3540m
(27) $K^{+}\,{}^{-}C(NO_2)_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO{\cdot}CH_3$	695m 747m 812w 848m	1020w 1102w 1122s *1176s*	1205m 1245m 1274m 1297m	[*1333*] [1360sh] s 1391w	1410w 1452w 1480s	1705s 3375m
(28) $K^{+}\,{-}C(NO_2)_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2CH_3$	751m 789w 857w 915m 971m	1014m [*1130*] [1096sh] s [1178] [1199]s [1211]	[1243] [1315] [1293] s [1268]	1350s 1379s	1440w 1480s	1740s 3295m

* Determined in KBr pellets, except for (3) which decomposed on pressing and was determined in Nujol and Fluorolube. Bands containing multiple maxima are in brackets (values in order of decreasing intensity). The two strongest bands in each spectrum are in italics.

TABLE 2

Infrared spectra (cm.$^{-1}$) of di-(2,2-dinitroethoxy)methane derivatives

(23) [a]	(24) [a]	(25) [a]	(29) [b]	(30) [c]	(31) [a]	(32) [a]	Associated with $-C(NO_2)_2^-$
715m	715m	710w	730m	705w	731m	718w	No
737w							
764m	752m	758m	772s	773m			Yes
	791m	800m	795s	815s	795m	799s	No
864w	857w	871w	849m	840w	838m	835m	Probably not
			874m	859m	888m		
921m	931m	932w	932s	915m	920m	910w	No
952w			969w		944m	972w	
1014s	1006s	1009s	1042s	992s	1008m	1000s	No
				1035s	1040s	1014s	
1075m	1073s	1074s	1093m	1088m	1107m	1104s	No
1144s	1123s	1112s	1134m	1125s	1117m	1137m	Uncertain
1174w	1163w	1176m	1180m	1178w	1168m	1170m	No
	1194w						
1230s	1217s	1209s					Yes
1250sh	1276s	1241s				1260w	Yes
1281w	1313m	1284m	1300s [d]	1305s [d]	1300s [d]	1295s [d]	Uncertain
1304m							
1339m	1356m	1342m	1338m	1339m	1340m	1340m	No
1370m	1389s	1358m				1380m	Yes
		1373m					
1420w	1420w	1416w	1410w	1408w		1410w	No
1497s	1492s	1471s					Yes
		1486s					
		1604w	1610s [e]	1600s [e]	1600s [f]	1595s [e]	No
		1690s [g]				1700s [g]	No

Compounds (23)—(25), see Table 1.
(29) $[C(NO_2)_3{\cdot}CH_2{\cdot}O]_2CH_2$. (30) $[CCl(NO_2)_2{\cdot}CH_2{\cdot}O]_2CH_2$. (31) $[CBr(NO_2)_2{\cdot}CH(CN){\cdot}O]_2CH_2$.
(32) $[CH(NO_2)_2{\cdot}CH(CONH_2){\cdot}O]_2CH_2$.

[a] Spectra on pressed KBr pellets. [b] Spectrum on Fluorolube and Nujol mulls. [c] Spectrum on liquid film. [d] Non-ionic nitro symmetrical stretch. [e] Non-ionic nitro asymmetrical stretch. Amide-II. [g] Amide-I.

(*b*) reference-compound absorption was clearly attributable at least in part to non-ionic nitro-groups, and (*c*) $-C(NO_2)_2^-$ absorption was to be expected at such positions. These questionable bands are denoted by a single diagonal mark through the bar.

Table 2 illustrates how the relatively complex spectra of compounds (23)—(25) were " cleaned up " in this way. Comparisons were made with the spectra of compounds (29)—(32).

Where comparison compounds were not readily at hand, the second approach involved a number of band assignments which could, with fair confidence, be made to other functionality by reference to the literature. Thus, for example, the 1074 and 1075 cm.$^{-1}$ bands (labelled "A" in Figure 1) of potassium 2-methoxy- and 2-ethoxy-1,1-dinitroethane (13 and 14) are almost certainly attributable to the C–O–C linkage.[6] The corresponding bands fall at 1073—1075 cm.$^{-1}$ in the salts (23)—(25) and at 1088—1107 cm.$^{-1}$ in the corresponding reference compounds (29)—(32) (Table 2). Similarly paralleled in all these compounds at 910—937 cm.$^{-1}$ (Table 2) are the 940 and 952 cm.$^{-1}$ bands of (13) and (14) (labelled " B "), also probably assignable to some C–O–C mode.[6]

Other such assignments were: C, the 1130 cm.$^{-1}$ band in compound (27), attributed to the secondary alcohol C–O stretch;[6] D, the 1405 cm.$^{-1}$ band in compound (19), assigned to the amide C–N stretch;[6] E, a strong shoulder at 1270 cm.$^{-1}$ in the zwitterion (26), attributable to the NH_3^+ symmetrical deformation;[6] F, the –CH=CH– *trans* hydrogen out-of-plane deformation at 962 cm.$^{-1}$ in (19).[6]

Elimination of most non-pertinent bands in the above ways left substantially smaller the number of spectral characteristics potentially attributable to the 1,1-dinitro-carbanion linkage. As may be seen in Figure 1, there appeared to remain five primary regions of absorption common to all or most of the twenty-nine salts.

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[6] L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," 2nd edn., Wiley, New York, 1958. Bands A and B, p. 116; C, p. 108; D, p. 220; E, p. 259; F, p. 45.

Deuteration Study.—To provide further guidance in band assignment, potassium deuterodinitromethane (2a) was prepared and its spectrum compared with that of the corresponding hydrogen compound (2) (Table 1, Figures 1 and 2). It was anticipated that band-positions would be affected in one of three ways on replacement of hydrogen by deuterium: (*a*) positions of maxima associated with N–O vibrations would remain unchanged or shift only slightly; (*b*) bands attributable to C–N vibrations would show markedly greater shifts; (*c*) bands deriving from C–H fundaments would either move to entirely new spectral regions or disappear completely from the measured spectrum (680—5000 cm.$^{-1}$).

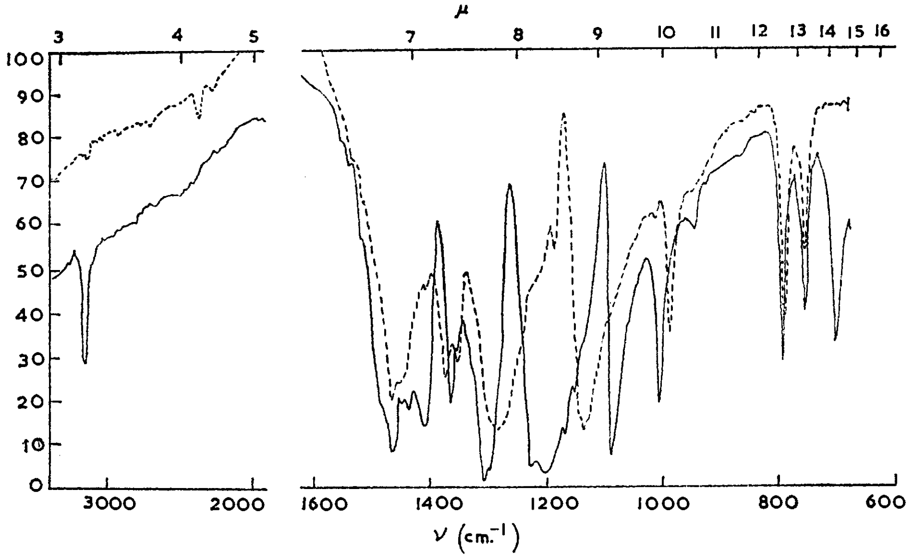
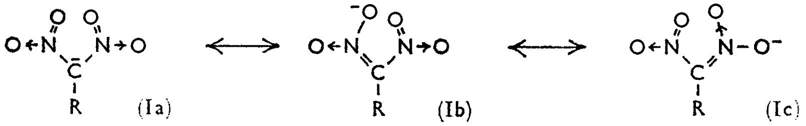


FIGURE 2. Spectra, in potassium bromide pellets, of potassium dinitromethane (solid line) and potassium deuterodinitromethane (broken line)

Into catageory (*a*) fell the following bands in (2) whose corresponding positions in (2a) are shown in parentheses: 1462 (1465); 1363 (1353); 1300 (1285); 1001 (980); 786 (781); 748 (750) cm.$^{-1}$. Category (*b*) included bands at 1407 (1370) and 1205 (1135) cm.$^{-1}$. Category (*c*) consisted of the C–H stretch at 3140 cm.$^{-1}$ in (2), shifted to 2380 cm.$^{-1}$ in (2a), as well as bands at 1081 and 694 cm.$^{-1}$ which disappeared completely.

DISCUSSION

It is profitable to preface a detailed discussion of the spectra with a review of some *a priori* considerations regarding the structures of 1,1-dinitro-carbanions. These compounds are considered [3,7] as being resonance hybrids incorporating varying contributions from the primary canonical structures (Ia—c).



(Ia) (Ib) (Ic)

Maximal resonance interaction would require total coplanarity, but oxygen–oxygen repulsions probably cause some skewing of the nitro-groups. Factors allowing expansion

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[7] M. J. Kamlet and D. J. Glover, *J. Org. Chem.*, 1962, **27**, 537.

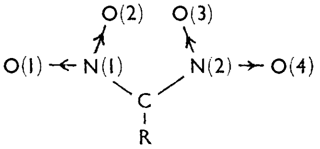
of the N–C–N angle and correspondingly decreased O–O repulsions should favour nitro coplanarity and lead to enhanced contributions from canonical structures (Ib) and (Ic); contraction of the N–C–N angle should have the converse effect. A number of physical and chemical properties of 1,1-dinitroalkanes and their carbanion salts are therefore quite sensitive to the steric requirements of R.

Thus, for example, a 6 p*K* unit increase in acidity from nitroform to dinitroacetonitrile [8] and a 1·6—2·0 p*K* unit increase from other 1,1-dinitroalkanes to dinitromethane [9] may be rationalised on the basis of an expanded N–C–N angle allowing greater coplanarity in the carbanion. Conversely, a twenty-fold decrease in acidity from unbranched 1,1-dinitroalkanes to 1,1-dinitro-2-methylpropane [9] may be regarded as attributable to a contracted N–C–N angle in the carbanion.

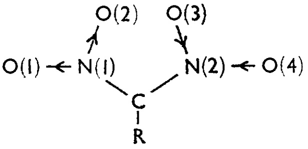
From ultraviolet spectra–structure correlations,[7] inductive electron-withdrawing substituents Z in $Z{-}CH_2{\cdot}C(NO_2)_2^-$ stabilise canonical structure (Ia) relative to (Ib) and (Ic); internal hydrogen-bonding from Z to nitro stabilises (Ib) and (Ic) relative to (Ia); and, by a field effect, unpaired electrons on the atom β to the dinitromethide function destabilise (Ib) and (Ic) relative to (Ia).

It is a consequence of the 1,1-dinitro-carbanion's tendency towards coplanarity that, unlike mononitro-carbanions or non-ionic *gem*-dinitro-compounds, the N–O bonds are not necessarily equivalent. The internal bonds N(1)–O(2) and N(2)–O(3) in (II) and (III) may be distinct from and may affect one another's force constants more strongly than the external bonds N(1)–O(1) and N(2)–O(4).

For this reason one must consider the strong possibility that, relative to other types of nitro-compound, new electronic and mechanical interactions may come to play. For example, (II) and (III) may evolve as spectrally distinct symmetrical vibrations of the individual nitro-groups or, indeed, in the form of some complex mechanical coupling pattern.



(II) sym(sym)



(III) asym(sym)

Such interactions should become increasingly significant with increasing coplanarity of the nitro-groups, and the surprisingly complex spectrum of potassium dinitromethane (2), the simplest compound studied, may derive in part from such effects. At least six bands of (2) seem associated with N–O vibrations.

Since all spectra were determined on solids, the position of the cation in the crystal lattice is another potential contributor to spectral variation which can neither be evaluated nor ignored. "Cation effects" may manifest themselves in several ways. With the individual compound, unsymmetrical positioning of the cation relative to the N(1)–O(1) and N(2)–O(4) bonds may contribute to nitro-group non-equivalence and thence to broadening or splitting of bands as discussed above. In comparing sets of compounds, differential positioning of the cation relative to the $-C(NO_2)_2^-$ grouping may also alter the stabilities, relative to one another, of the canonical resonance structures corresponding to (Ia), and (Ib) and (Ic). Thus shifts might be caused in band positions, which, lacking twenty-nine total-crystal-structure determinations, would be completely unpredictable and essentially independent of the nature of R.

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[8] T. N. Hall, *J. Org. Chem.*, 1964, **29**, 3587.

[9] S. S. Novikov, V. M. Belikov, A. A. Feinzil'berg, L. V. Ershova, and S. A. Shevelev, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1855; A. Hantzsch and A. Veit, *Ber.*, 1899, **32**, 607; J. S. Belew and L. G. Hepler, *J. Amer. Chem. Soc.*, 1956, **78**, 4005.

Novikov and his co-workers [3] provide data which illustrate the magnitude of such "cation effects." In the series lithium, ammonium, sodium, and potassium dinitromethane, positions of the maxima for the three bands reported differed by as much as 37, 37, and 25 cm.$^{-1}$. With ammonium, sodium, and potassium 1,1-dinitroethane, differences were as high as 28, 22, and 17 cm.$^{-1}$, and with ammonium, sodium, and potassium 1,1-dinitropropane, 3, 9, and 15 cm.$^{-1}$.

In the face of these complications, any attempt at relating band-position variations in $R-C(NO_2)_2^-K^+$ to the nature of R must be with the full understanding that unpredictable factors independent of R may be over-riding. Hopefully, however, if averages are taken for sufficient structurally related compounds, such R-independent variables might cancel one another out and trends then become discernible.

Band I, the Nitro Asymmetrical Stretch.—This band is of strong intensity in all twenty-nine salts, and, being reasonably isolated, is the most readily identified in the typical 1,1-dinitro-carbanion spectrum. Its average position is 1482 ± 10 cm.$^{-1}$, extreme positions being 1516 (compound 1) and 1442 (4). Excluding from consideration compounds (1)—(5), which might have somewhat dissimilar steric requirements about the dinitromethide linkage, $\nu_{av.}$ becomes 1484 ± 6 cm.$^{-1}$ with extremes of 1470 (19) and 1497 (23).

We attribute this absorption to the nitro asymmetrical stretching vibration. The assignment follows primarily from a consideration of how nitro asymmetrical stretching frequencies vary with C–N bond-orders for other classes of nitro-compound.*

Aliphatic nitro-compounds show this valence vibration in the range 1630—1530 cm.$^{-1}$, higher frequencies being common to compounds with a plurality of electron-withdrawing groups about the C–nitro linkage, *e.g.*, tetranitromethane [10] 1618, chlorotrinitromethane [11] 1617, trichloronitromethane [1] 1610 cm.$^{-1}$. C–N bond-orders are 1·0 in such compounds, or lower if canonical structures $X_3C^-\ {}^+NO_2$ are significant resonance contributors.[1]

Electron-releasing groups shift aliphatic nitro maxima in the converse direction, *e.g.*,[1] alkyl-$CH_2{\cdot}NO_2$ 1560 ± 15, $(alkyl)_2CH{\cdot}NO_2$ 1550 ± 15, $(alkyl)_3C{\cdot}NO_2$ 1540 ± 10 cm.$^{-1}$. Bond-orders in such compounds would tend to increase as the C–N linkage assumed partial double-bond character with contributions [1] from canonical resonance structures $R^+\ R_2C{=}NO_2^-$.

In the aromatic series the corresponding vibrations lead to absorption in the range 1560—1500 cm.$^{-1}$. A ρ-σ relationship has been observed [12] wherein electron-releasing substituents again cause shifts to lower frequencies. Such substituents should increase significance of resonance contributors $[{}^+X{=}C(4) \longrightarrow C(1){=}NO_2^-]$ and correspondingly increase C–N bond-orders. Trotter [13] has suggested values around 1·3 as reasonable for bond-orders in unhindered aromatic nitro-compounds.

The apparent trend toward lowered asymmetrical nitro stretching frequencies with increasing C–N bond-order is carried toward the extreme with the mononitro-carbanion salts. Jonathan [14] reported these vibrations at 1163 and 1176 cm.$^{-1}$ for sodium 2-nitropropane, and at 1263 and 1278 cm.$^{-1}$ for sodium nitromethane. Feuer, Savides, and Rao [15] attributed bands in the region 1316—1225 cm.$^{-1}$ to this mode in a series of nine primary and secondary mononitroalkane sodium salts. C–N bond-orders have been estimated as 1·88 for sodium nitromethane, and 1·80 for sodium 2-nitropropane.

Figure 3 shows variation in asymmetrical nitro stretching frequency with C–N bond-order for these four classes of nitro-compounds. The following rough, but self-consistent,

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* The variation with N–O bond-orders would, of course, be more meaningful. It is expected, however, that the latter would show a regular inverse relationship with C–N bond-orders.

[10] P. Lindenmeyer and P. Harris, *J. Chem. Phys.*, 1953, **21**, 408.

[11] V. I. Slovetskii, A. A. Feinzil'berg, V. I. Gulevskaya, and S. S. Novikov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 683.

[12] R. D. Kross and V. A. Fassel, *J. Amer. Chem. Soc.*, 1956, **78**, 4225.

[13] J. Trotter, *Canad. J. Chem.*, 1959, **37**, 905.

[14] N. Jonathan, *J. Mol. Spectroscopy*, 1961, **7**, 105.

[15] H. Feuer, C. Savides, and C. N. R. Rao, *Spectrochim. Acta*, 1963, **19**, 431.

bond-order estimates were used: X_3CNO_2 (X = NO_2 or Hal), 0·9—1·0; R_3CNO_2 (R = H or alkyl), 1·05—1·15; nitro-aromatics, 1·25—1·35; mononitro-carbanion salts, 1·8—1·9.

Depending on relative contributions of canonical resonance structures (Ia), and (Ib) and (Ic) to the total structures, 1,1-dinitro-carbanion (C–N bond-orders must fall between the limits 1·0 and 1·5. Judging from properties and reactivity, the range 1·35—1·45 seems reasonable.*

It is evident from Figure 3 that the 1516—1442 cm.$^{-1}$ range of band I is fully consistent with such bond-order estimates. More important, however, if the above relationship obtains, the lower frequency ranges of bands II—V are inconsistent with any 1,1-dinitro-carbanion bond-order estimate below the allowable limit of 1·5. Thus, by elimination, this asymmetrical mode must be assigned to band I.

The isotope study provided confirmation for the assignment. As would be expected for N–O valence vibrations, replacement of hydrogen by deuterium in potassium dinitromethane left the position of this band essentially unchanged, 1462 cm.$^{-1}$ in (2), 1465 in (2a).

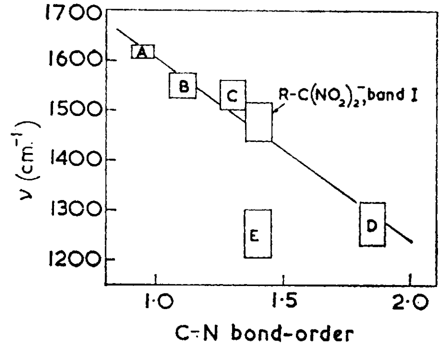

FIGURE 3. Nitro asymmetrical stretching frequency as a function of C–N bond-order. A, X_3CNO_2 (X = NO_2 or Hal); B, R_3CNO_2 (R = H or alkyl); C, nitro-aromatics; D, mononitrocarbanion salts; E, 1,1-dinitro-carbanion band III, attributed by Brown and by Kaplan to nitro asymmetrical stretch

In view of the above findings, it appears necessary to re-examine a comment by Novikov and his co-workers [3] to the effect that 1,1-dinitro-carbanion spectra do not contain "bands corresponding to the nitro-group in true nitro-compounds." The band I range recorded here overlaps slightly that reported for the asymmetrical nitro stretch in nitro-aromatics,[1,12] *e.g.*, (1) 1516, (5) 1505, *p*-nitrophenol 1515, *p*-nitroaniline 1504, sodium *p*-nitrophenoxide 1501 cm.$^{-1}$. Indeed, one might conclude from the present results that charge distributions over the individual nitro-groups in dinitro-carbanions do not differ markedly from those in highly conjugated nitro-aromatics. Further, the fact that the band shift is not appreciable from *p*-nitrophenol, a "true nitro-compound," to sodium *p*-nitrophenoxide with full formal charge, lends confidence to our relating mono- and di-nitro-carbanion spectra to those of non-ionic compounds.

As concerns variation of band I $\nu_{max.}$ with R in $R-C(NO_2)_2^-$, the situation is less clear-cut. It has been mentioned that conjugating substituents should lead to lower C–N bond-orders. This would have the effect of shifting maxima to higher frequencies, as appears to be the case with the potassium salts (1) 1516, (5) 1505, and (18) 1493 cm.$^{-1}$, and with potassium 1,3,3-trinitroprop-1-ene for which $\nu_{max.}$ (Nujol) 1499 cm.$^{-1}$ has been reported.[16] The effect is not apparent, however, with (17), 1480 cm.$^{-1}$, or (19), 1470 cm.$^{-1}$. It may be that in the latter instances "cation effects" or other factors are over-riding.†

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* For compounds (1), (5), and possibly (17)—(19), the probable value would be somewhat lower owing to delocalisation of charge over the additional conjugating group, *e.g.*:

$$^{-}O-C(OMe)=CH=CH=C(NO_2)_2.$$

† To explain the fact that (17)—(19) each show two main bands above 300 mμ in the ultraviolet, it has been suggested [7] that with these compounds coplanar and non-coplanar rotomers are of comparable energy, both forms coexisting in appreciable amounts in aqueous solution. It may also be that (18) crystallises as the coplanar rotomer, and (17) and (19) in the non-coplanar form.

[16] M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *J. Org. Chem.*, 1961, **26**, 4881.

It has also been suggested [7] that unpaired electrons on the atom β to the dinitromethide function destabilise resonance structures (Ib) and (Ic) relative to (Ia), which should again lead to lower C-N bond-orders and absorption at higher frequencies. Six salts (13—15 and 23—25) with unpaired electrons on the β-atom and incapable of internal hydrogen-bonding (which should have a converse effect) show $\nu_{av.}$ 1491 ± 3 cm.$^{-1}$; eight 1,1-dinitroalkane or 3-substituted 1,1-dinitropropane salts (6—11, 27, 28) show $\nu_{av.}$ 1481 ± 4 cm.$^{-1}$.

Conversely, pile-up of charge on neighbouring atoms in dipotassium 1,1,2,2-tetranitroethane (20) and dipotassium 1,1,3,3-tetranitropropane (21) should destabilise structures (Ia) relative to (Ib) and (Ic), thus leading to higher C-N bond-orders and absorption at lower frequencies. These compounds show $\nu_{max.}$ 1478 and 1472 cm.$^{-1}$, respectively.

No satisfactory explanation is at hand for the low band I frequencies of potassium chloro- (3) and bromo-dinitromethane (4) at 1452 and 1442 cm.$^{-1}$. On steric or electronic grounds, C-N bond-orders would be expected to be lower for these compounds than with the typical dinitro-carbanion, and absorption should be expected at correspondingly higher frequencies.

Band II.—Medium to strong bands between 1300 and 1400 cm.$^{-1}$ have generally been ignored by earlier investigators of 1,1-dinitroalkane salt spectra,[1,4] possibly because they had been attributed to hydrogen deformation frequencies in CH_3 or CH groups which absorb in this range.[6] We have found, however, that a characteristic band probably attributable to $-C(NO_2)_2^-$ appears in this region even when such hydrogen deformations are excluded. Because the region is more crowded, exact identification of the dinitro-carbanion band II is somewhat more difficult than was the case with band I, and the choices shown in Figure 1 may in some cases be subject to doubt.

The average position for the twenty-nine salts is 1360 ± 17 cm.$^{-1}$, extremes being 1430 (5) and 1333 cm.$^{-1}$ (27). Excluding compounds (1)—(5), $\nu_{av.}$ becomes 1352 ± 14 cm.$^{-1}$ with extremes of 1389 (24) and 1333 (27).

The deuteration study provided little help in band assignment. Potassium dinitromethane (2) shows two bands in this range (Figure 2). A maximum at 1407 cm.$^{-1}$ underwent a marked shift to 1373 on deuteration; another at 1363 cm.$^{-1}$ shifted only slightly to 1353. There is no basis for judging which of these corresponds to band II.

For this reason, and because no obvious generalisations were possible regarding variation of $\nu_{max.}$ with structure, we leave the band II assignment problem unresolved other than to suggest the likeliest possibilities, an N-C-N asymmetrical stretching frequency (see discussion of band IV) or a nitro stretching frequency arising from such possible new coupling patterns as represented by II or III.

Band III, the Nitro Symmetrical Stretch.—With the inclusion of additional types of 1,1-dinitro-carbanion salts, the range of variation for this high-intensity band becomes markedly greater than the 1240—1273 cm.$^{-1}$ reported by Kaplan.[2] Again subject to the qualification that spectral crowding in this region sometimes leads to ambiguity in the exact identification of band III, the average position for twenty-nine salts is 1252 ± 17 cm.$^{-1}$, extreme positions being 1205 (3) and 1300 (2). Excluding compounds (1)—(5), $\nu_{av.}$ becomes 1250 ± 13 cm.$^{-1}$, with extremes of 1218 (14) and 1293 (12).

As with band I, our attributing this absorption to a nitro valence vibration is strengthened by the fact that the band position is not shifted markedly on deuteration of potassium dinitromethane, $\nu_{max.}$ being 1300 cm.$^{-1}$ in (2), and 1285 in (2a) (Figure 2). Further, the band falls in a region such as would be expected for the nitro symmetrical stretch from a consideration of the corresponding band positions in non-ionic nitro-compounds and mononitro-carbanions.

For nitroalkane derivatives this vibration leads to absorption at frequencies ranging from 1375 to 1310 cm.$^{-1}$, and with nitro-aromatics the range 1351—1315 has been reported.[1,12] Several workers have commented that plots of nitro symmetrical *versus* nitro asymmetrical stretching frequencies are non-linear in both the nitro-aromatic and the nitro-aliphatic series.[1,12]

There is also rough agreement regarding nitro symmetrical stretching position in mononitro-carbonion spectra. Jonathan [14] suggested this assignment for sodium nitromethane bands at ~1025 and sodium 2-nitropropane bands at ~950 cm.$^{-1}$. Feuer and his co-workers [15] made similar attributions to band systems at 1175—1015 cm.$^{-1}$ in their primary and secondary mononitroalkane salts.

As with band I, a mid-point between the ranges reported for non-ionic nitro-compounds and those for mononitro-carbanions would seem appropriate for the symmetrical stretching frequencies of 1,1-dinitro-carbanion salts. Of the five bands, band III appears best to satisfy this requirement.

An interesting feature of band III (and of band IV to a lesser extent) is the marked variation in band-width, ranging from 70—105 cm.$^{-1}$, for the dinitromethane derivatives (1)—(5) and the dipotassium salt (20), to 20—30 for the 3-substituted 1,1-dinitropropane and propene derivatives (9)—(11) and (17)—(19). These differences and the band-splittings in compounds (13), (16), (21), (27), and (28) may result from such interactions as we have suggested might lead to non-equivalence of nitro-groups or of N–O bonds within the individual nitro-group.

Band IV, and N–C–N *Stretching Vibration.*—Although often the strongest in the spectrum, this band presents the greatest difficulty in exact identification. The broad range, 1220—1105 cm.$^{-1}$, overlaps that of band III, and at least eleven compounds have two or even three not otherwise assigned maxima within the spectral region under consideration. Nor does there seem to be any regular variation of $\nu_{\text{max.}}$ with structure or with the positions of other bands. For these reasons the band IV attributions in Figure 1 are subject to scepticism as are the values $\nu_{\text{av.}}$ (compounds 1—28) = 1154 ± 28 cm.$^{-1}$ and $\nu_{\text{av.}}$ (6—28) = 1155 ± 22 cm.$^{-1}$.

From the fact that deuteration caused the maximum at 1205 cm.$^{-1}$ in (2) to shift markedly to 1135 in (2a), we assign band IV to an N–C–N stretching vibration.*

We have mentioned the possibility that band II also derives from an N–C–N stretching vibration. If this is indeed the case, analogy with other geminally-substituted groupings [6] would suggest that the lower-frequency band IV be assigned to the N–C–N symmetrical stretching vibration, and the higher-frequency band II to the antisymmetrical stretching vibration.

Agreement seems general regarding carbon–nitrogen stretching frequencies of non-ionic nitro-aliphatic compounds of low C–N bond-order. Buczkowski and Urbanski [17] report 853—875, Haszeldine [18] 830—920, and Randle and Whiffen [19] ~850 cm.$^{-1}$. With mononitro-carbanion salts of C–N bond-order ~1·8—1·9,[14] the range 1587—1622 cm.$^{-1}$ is also generally agreed upon.[14,15,17] In the case of nitro-aromatics of intermediate C–N bond-order, no firm attributions have been made, although Kross and Fassel's suggestion [12] of ~1300 cm.$^{-1}$ for nitrobenzene may have merit.

One may conclude, therefore, that carbon–nitrogen stretching frequencies will depend strongly upon bond-orders and may range widely over the spectrum. The regions ~1360

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* It should be noted that we differ from Novikov and his co-workers [3] in the manner in which we relate potassium dinitromethane maxima to those of the other 1,1-dinitroalkane salts. In our view the 1300 cm.$^{-1}$ band corresponds to band III, the 1205 cm.$^{-1}$ to band IV, and the 1081 cm.$^{-1}$ maximum derives from a C–H fundamental. The Russian workers relate the 1081 cm.$^{-1}$ maximum (observed by them at 1090 cm.$^{-1}$) to band IV, the 1205 cm.$^{-1}$ maximum (1225 cm.$^{-1}$) to band III, and they do not mention the 1300 cm.$^{-1}$ maximum. Based on the Novikov assignments, band IV shifts from 1081 to 1135 cm.$^{-1}$ on deuteration, band III from 1205 to 1285 cm.$^{-1}$, and the 1300 cm.$^{-1}$ band disappears. It is difficult to rationalise a shift of two bands to *higher* frequencies as would be the case if Novikov's assignments were correct. It is further noteworthy that, based on either set of assignments, the deuteration results are inconsistent with the Brown–Kaplan band-attributions.[1,2]

[17] Z. Buczkowski and T. Urbanski, *Spectrochim. Acta*, 1962, **18**, 1187.
[18] R. N. Haszeldine, *J.*, 1953, 2525.
[19] R. R. Randle and D. H. Whiffin, *J.*, 1952, 4153.

and ~1154 cm.$^{-1}$ for the N–C–N asymmetrical and symmetrical stretching frequencies of 1,1-dinitro-carbanion salts with C–N bond-orders 1·34—1·45 are not inconsistent with such a picture.

Band V.—This variable-intensity band falls within a comparatively narrow range. For the twenty-nine salts, $\nu_{av.} = 746 \pm 9$ cm.$^{-1}$. Excluding potassium chloro- and bromo-dinitromethane (3 and 4), $\nu_{av.}$ becomes 749 ± 5 cm.$^{-1}$. The band is not particularly useful for identification because all nitro-compounds show absorption in the general region. We believe that this band (position unchanged on deuteration of 2) derives from a nitro bending mode.

TABLE 3

Characteristic bands of 1,1-dinitro-carbanion salts

Band	Range (cm.$^{-1}$)	$\nu_{av.}$ (cm.$^{-1}$)	Assignment
I	1516—1442	1482 ± 10	Nitro asymmetrical stretch
II	1430—1333	1360 ± 17	Possibly N–C–N asym. stretch
III	1300—1205	1250 ± 13	Nitro symmetrical stretch
IV	1220—1105	1154 ± 28	N–C–N stretch, possibly sym.
V	764—715	746 ± 9	Nitro bending

EXPERIMENTAL

Spectra were determined on pressed potassium bromide pellets. (CAUTION) Since these compounds are explosive and many are particularly sensitive to friction, extreme care was exercised in grinding them.

Most of the 1,1-dinitro-carbanion salts were prepared by published procedures.[5,7,20,21] The syntheses of the salts (23)—(25), their reference compounds (29)—(32), and the hydroxy-compounds (27) and (28) will be reported in forthcoming publications from these laboratories. Potassium deuterodinitromethane (2a) was prepared by the reduction of dibromodinitromethane with arsenic trioxide in potassium hydroxide–deuterium oxide, following the procedure of Duden.[22] Exchange of any residual hydrogen was accomplished by recrystallising the material twice from deuterium oxide.

Potassium chlorodinitromethane (3) decomposed under the conditions of pressing. The spectrum of this material was determined in Nujol and Fluorolube mulls.

A Beckman IR-4 recording spectrophotometer fitted with sodium chloride optics was used to determine the spectra, generally between 680 and 4000 cm.$^{-1}$. The reported band positions were corrected with the help of calibration spectra taken on standard polystyrene film.

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[20] R. A. Gotts and L. Hunter, *J.*, 1924, **125**, 442.
[21] M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, 1963, **28**, 2128.
[22] P. Duden, *Ber.*, 1893, **26**, 3004.