gave bright red crystals which resisted purification; the best sample had a nitrogen content indicating a mixture of about equal parts of the furoxan and the azine. As indicated above, more heavily substituted diaroylfuroxans gave no indication of reaction even in the presence of alkali.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

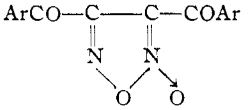
The Infrared Absorption Spectra of Furoxans[1]

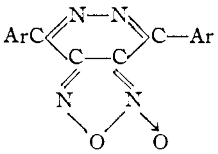
BY N. E. BOYER, GLORIA M. CZERNIAK, H. S. GUTOWSKY AND H. R. SNYDER

RECEIVED MARCH 31, 1955

The infrared absorption spectra of a number of diacylfuroxans, of some bicyclic azines obtained from such diacylfuroxans and hydrazine, and of some more simply substituted furoxans have several unique regions of absorption in the range of 1800–800 cm.$^{-1}$. Certain of the absorption bands are assigned to particular vibrations of the furoxan structure. The use of the spectra in the identification of furoxans is discussed.

As a part of a general study of the properties of furoxans,[2] we have investigated the infrared absorption spectra of a number of diacylfuroxans (I), of some of the bicyclic azines (II) obtained from them by reaction with hydrazine, and of several more simply substituted furoxans. The interest in these spectra was twofold. They should provide data for the empirical assignment of the characteristic absorption frequencies of the furoxan ring and thus be of use in structure determination, and the characteristic frequencies and their variations upon substitution should eventually permit a better understanding of the electronic nature of the furoxan system and of its interaction with substituents. At the time these studies were made no infrared absorption data for furoxans had been published, although the spectra of some furazans, azoximes and oxadiazoles were available.[3] Recently, the spectra of benzfuroxan and some of its derivatives were reported.[4]


I


II

In the present work, the spectra of the various compounds exhibited no absorption bands characteristic of the furoxan group within the ranges 4000–1800 cm.$^{-1}$ and 800–625 cm.$^{-1}$. However, several regions of absorption in the range 1800–800 cm.$^{-1}$ are peculiar to the furoxan ring. These regions are listed in Table I with tentative vibrational assignments. Each of these regions is discussed in some detail below.

The spectra of all the furoxans as well as of the benzfuroxans,[4] have a consistently strong absorption band in the 1625–1600 cm.$^{-1}$ region. This is the double bond stretching region and since the only double bonds in dimethylfuroxan are C=N, this assignment is made. One might expect different frequencies for the $\mathrm{C{=}N{\rightarrow}O}$ and C=N—O sides of the ring; however, the evidence on this point is not conclusive. An appreciable fraction of the spectra have a weak to strong band in the 1600–1500 cm.$^{-1}$ region which could be a second C=N stretching frequency. A comparison of the spectra of the furoxans with those of the furazans[4] suggests that the 1625–1600 cm.$^{-1}$ band is associated with the presence of the $\mathrm{C{=}N{\rightarrow}O}$ group. This view is supported by the relative insensitivity of the band to substituents, which contrasts with the wide ranges found for C=N bands in other compounds.[5]

The absorption occurring as a doublet in the 1475–1410 cm.$^{-1}$ region is easily discernible in compounds without methyl groups, which absorb in the same region. In some compounds, such as bis-(*m*-nitrobenzoyl)-furoxan, the azine of bis-(5-methyl-3-isoxazolecarbonyl)-furoxan and furoxandicarboxamide, interference by Nujol resulted in the occurrence of one broad band when samples were examined as mulls. However, even in most such instances the lower vibration of the doublet could be detected. A characteristic band in the 1360–1300 cm.$^{-1}$ region, of medium to very strong intensity, is masked by the absorption of nitro groups in compounds which bear this group as a substituent. In some instances, such as bis-(*m*-nitrobenzoyl)-furoxan and bis-(*p*-nitrobenzoyl)-furoxan, the composite band is split as the absorption by the nitro group shifts to higher frequencies. In only one spectrum, that of the azine of bis-(*p*-chlorobenzoyl)-furoxan was there no indication of absorption in this range; all the bands in this spectrum were weak. Since neither Nujol nor chloroform interferes in the 1360–1300 cm.$^{-1}$ region, the strong absorption here should be useful in the identification of furoxans which do not bear nitro groups as substituents.

A summary of the absorption bands in the 1475–1410 cm.$^{-1}$ and 1360–1310 cm.$^{-1}$ regions is given in Table II. This table includes all the samples having no conflicting methyl or nitro groups, and is based on spectra determined in chloroform solution to avoid interference by Nujol. The similarity of these absorption bands to those of the nitro

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[1] The synthesis of the furoxans studied was carried out under a sub-contract with Arthur D. Little, Inc., under contract DA-19-020-ORD-47 with the Office of the Chief of Ordnance. The manuscript has been approved for publication by the Office of Public Information, Department of Defense.

[2] H. R. Snyder and N. E. Boyer, THIS JOURNAL, **77**, 4233 (1955).

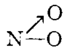
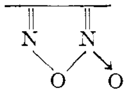
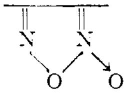
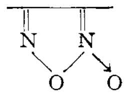
[3] M. Milone and E. Borello, *Gazz. chim. ital.*, **81**, 368 (1951).

[4] R. J. Gaughran, J. P. Picard and J. V. R. Kaufman, THIS JOURNAL, **76**, 2233 (1954).

[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 226.

TABLE I

INFRARED ABSORPTION BANDS CHARACTERISTIC OF THE FUROXANS

Range of absorption, cm.$^{-1}$	Probably due to the following bonds or groups	Appearance of the absorption bands is limited to the following types	Other functional groups or solvents which interfere
1625–1600	C=N	All furoxans studied	
1475–1410 (doublet)	 $\mathrm{N}\begin{smallmatrix}\nearrow\mathrm{O}\\ -\mathrm{O}\end{smallmatrix}$	All furoxans studied	Methyl groups Nujol
1360–1300	N-O	All furoxans studied	Nitro groups
1190–1150		All furoxans studied	Ethyl, isopropyl (m); benzenoid rings (w); ether groups (s)
1030–1000		All furoxans studied	
950–900	Diaroylfuroxans, their carbonyl derivatives (*e.g.*, azines) Diarylfuroxans	Furoxans with benzenoid groups in the side chains	
890–840		All furoxans studied	

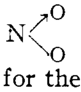
group, occurring at 1540 and 1350 cm.$^{-1}$, suggests that they are characteristic of the nitrogen–oxygen linkages of the furoxan group. The latter bonds have less double bond character than those in the nitro group. This would decrease the vibrational frequencies, as observed. There is some evidence that the  $\mathrm{N}\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{O}\end{smallmatrix}$ part of the furoxan group is responsible for the doublet at 1475–1410 cm.$^{-1}$ while the N–O gives the absorption at 1360–1310 cm.$^{-1}$. The furazans have N–O bonds but not the N→O feature; and they absorb[3] in the region in question only at the lower values 1430–1385 cm.$^{-1}$.

TABLE II

SUMMARY OF FUROXAN ABSORPTION IN THE 1475–1410 CM.$^{-1}$ AND 1360–1310 CM.$^{-1}$ REGIONS

Furoxan	Absorption bands, cm.$^{-1}$	
Dibenzoyl-	1475s	1340s
	1460s	
Bis-(*p*-chlorobenzoyl)-	1480s	1332s
	1450m	1290m
	1410s	
Bis-(*p*-phenylbenzoyl)-	1480m	1330s
	1455m	
	1415m	
Azine of dibenzoyl-	1458s	1357m
	1440s	1315w
Azine of bis-(*p*-chlorobenzoyl)-	1445s	None
	1420m	
Azine of bis-(*p*-phenylbenzoyl)-	1455s	1335m
	1415m	

Absorption in the 1250–1200 cm.$^{-1}$ region was noted in the spectra of all the furoxans examined except dimethylfuroxan and furoxandicarboxamide. Its absence in these instances indicates that this band is not a furoxan absorption. It is strong in compounds containing benzene rings conjugated with carbonyl groups or with C=N— groups (in the azines), and in compounds having carbon-oxygen linkages as well as a multiplicity of carbon–carbon bonds. Therefore, the absorption is probably a composite of carbon–oxygen and/or carbon–carbon stretch, intensified by the aromatic ring or the carbon–oxygen or carbon–nitrogen bonds.

Consistent correlations were found in four regions within the 1200–800 cm.$^{-1}$ range. Sharp, narrow bands in the regions 1190–1150, 1030–1000 and 890–840 cm.$^{-1}$, too far removed from the usual ranges of absorption by methyl groups to be caused by them, were noted in the spectra of all the furoxans studied. These bands probably result from bending vibrations and as such are more characteristic of the furoxan ring as a whole than of any specific part. The fourth band, usually a doublet, at 950–900 cm.$^{-1}$ was observed in the spectra of all the samples except dimethylfuroxan, furoxandicarboxamide and ethyl furoxandicarboxylate. The absence of this absorption in these instances suggests that it results from an interaction between the furoxan ring and unsaturated (C=O or C=N—) and aromatic substituents. The presence of this absorption is a good indication of the identity of an unknown as a diaryl or diaroylfuroxan, or an azine of the latter, since the probability of interference or masking in this region is low.

Interactions between substituents and the furoxan system cause characteristic displacements of several absorption bands. For example, conjugation of the double bonds of the furoxan ring with the carbonyl group in the diaroylfuroxans lowers the C=O frequency from the usual region,[6] 1700–1680 cm.$^{-1}$, to values as low as 1660 cm.$^{-1}$ and the absorption frequency of the carbonyl group in esters is displaced downward by about 10 cm.$^{-1}$. The effects of substituents on the furoxan frequencies are illustrated by the data in Table II for the doublet in the 1475–1410 cm.$^{-1}$ region. The frequencies for the dibenzoyl derivatives are consistently about 15 cm.$^{-1}$ higher than for the corresponding azine compounds. This implies that conjugation of the carbonyl group with the furoxan ring, while lower-

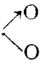
(6) Reference 5, p. 119.

TABLE III

CORRELATION OF VIBRATIONS DUE TO THE FUROXAN RING

Substd. furoxan	Furoxan	Medium tested in	Vibrations[a]							Comments[b]
1	Azine of dibenzoyl-	Nujol	1612s	1458s 1440s	1357m 1335w 1315w	1185m	1005s	930m 924m 904m	844vw	
2a[c]	Azine of bis-(*m*-nitrobenzoyl)-	Nujol	1615s	1452m 1405w	Mask by NO_2	1175vw	1015w	930m 914s	870m 855m	Made from 12a and hydrazine
3	Azine of bis-(*p*-nitrobenzoyl)	Nujol	1602s	1415m	1322m Partial mask by NO_2	1175vw	1025m	910m 875m	855s	
4	Azine of bis-(*p*-chlorobenzoyl)-	Nujol, chloroform	1605s	1452s 1415m	None	1180m	1020m	946m 920w	852m	
5	Azine of dianisoyl-	Nujol	1603s	Mask by CH_3 1430m	1335m	1175s	1015m	925m 899m	848m	Contains an impurity (compd. 20)
6	Azine of bis-(*p*-phenylbenzoyl)-	Nujol	1606s	1455s 1415m	1335s	1190m	1010m	925m 895s	850m	Contains an impurity (compd. 11)
7	Azine of bis-(5-methyl-3-isoxazolecarbonyl)-	Nujol, chloroform	1610s	Mask by CH_3, Nujol 1405vw	1352s	1160m	1010m	930s 904m	875m	From 23 and hydrazine dihydrochloride
8	Dibenzoyl-	Nujol, chloroform	1620s 1602s	1475s 1460s	1330s	1188m	1030m 1005m	930s 900s	850vw	M.p. 87°
9	Isomer of dibenzoyl-	Nujol	1610s	1425m	1335m 1315w	1185m	1040m 1005s	970m 905s	840w	M.p. 179°; described by Holleman[d]
		Chloroform	1610s	1430m	1335s 1315m	1185s	1040m 1005s	965m 902s	840w	
10	Bis-(*p*-chlorobenzoyl)-	Nujol, chloroform	1624s	1480s 1450m 1410s	1332s 1290m	1180m	1016m	936s 900s	850s	
11	Bis-(*p*-phenylbenzoyl)-	Nujol, chloroform	1607s	1455s 1415m	1335s	1190m	1010m	926m 896s	849m	
12a[e]	Bis-(*m*-nitrobenzoyl)-	Nujol	1620s	Mask by Nujol	1340s	1170w	1030vw	955m 930s 912m	870m	Made from *m*-nitroacetophenone and HNO_3
13	Bis-(*p*-nitrobenzoyl)-	Nujol	1625s 1610m	Mask by Nujol 1415w	1326s	1070w	1017m	944s 905s	860s	
14	Bis-(2,4-dimethylbenzoyl)-	Nujol	1615s	Mask by CH_3	1328s 1300w	1160w	1045m 1022m	955m	880s	
15	Dimesitoyl-	Nujol	1614s	Mask by CH_3 1430m	1310s	1168m	1035m	958m 900m	880s 855s	
16	Bis-(2,4-dimethyl-3,5-dinitrobenzoyl)-	Nujol	1620m	Mask by CH_3 1426m	1305s 1282m	1172m	1015w	920s 905m	865m	
17	Bis-(2,4,6-trimethyl-3,5-dinitrobenzoyl)-	Nujol	1612s	Mask by CH_3	1310s	None	1030m	932s 900s	875s	
18	Bis-(2,4,6-trimethyl-3-bromobenzoyl)-	Nujol	1613s	Mask by CH_3 1422m	1310s	1176m	1024m 990s	950m 903s	889s	
19	Bis-(2,4,6-triisopropylbenzoyl)-	Nujol, chloroform	1610s	1468s 1430m	1307m	1180w	Mask by $CHCl_3$	950m 915m	888s	
20	Dianisoyl-	Nujol	1610s	Mask by CH_3 1430m	1335s 1310m	1175s	1015s	926s 900s	848s	
21	Ethyl furoxandicarboxylate	Chloroform smear	1632s	Mask by CH_3	1335s 1305m	1175m	1030s	None	860s	
22	Benzyl furoxandicarboxylate	Nujol	1580s	Mask by Nujol 1420s	1305s	1165s	1014s	951m 911s	860m	Reacn. product of 21 and benzyl alc. in presence of sodium methoxide; impure sample
23	Bis-(5-methyl-3-isoxazolecarbonyl)-	Nujol, chloroform	1607s	1455s 1417m	1315s	1170m	1012m	940m 910s	875m	
24	Furoxandicarboxamide	Nujol	1610m	Mask by Nujol	1330s	1150m	1030s	None	855s	
25	Dimethyl-	Smear	1620s	Mask by CH_3	1305m	1170s	1045m 1000m	None	852m	Made from dimethylglyoxime and nitrogen dioxide in abs. ether
26a[f]	Bis-(*m*-nitrophenyl)-	Nujol	1600s	1410m	Mask by NO_2 1314w	1185vw	1020m 1003m	915m 910m	880s	Made from *m*-nitrobenzaldoxime and isoamyl nitrite
27	Disemicarbazone of bis-(*m*-nitrobenzoyl)-	Nujol	1617m	1410m	Mask by NO_2 1292m	1180w	None	980s 930w	858m	Prepared from 2a and semicarbazide

[a] s = strong; m = medium; w = weak; vw = very weak. [b] The method of preparation has been indicated in this column for those samples the synthesis of which has not been described in the preceding article[2] or where several methods were used. [c] Sample 2b was made from 12b and hydrazine, and had an identical spectrum to that of 2a. [d] A. F. Holleman, *Ber.*, **21**, 2840 (1888). [e] Sample 12b was made from dibenzoylfuroxan and fuming nitric acid in sulfuric acid, and showed an identical spectrum to that of 12a. [f] Sample 26b (prepared from *m*-nitrobenzhydroxamyl chloride and silver benzoate) and sample 26c (from *m*-nitrobenzhydroxamyl chloride and aqueous potassium hydroxide) showed an identical spectrum to 26a, and were also identified as bis-(*m*-nitrophenyl)-furoxan by mixed melting points (m.p. 184°).

ing the carbonyl frequency, increases the  frequencies.

Experimental

The infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer equipped with a sodium chloride prism. The samples were observed as mulls of the solid in Nujol or, when soluble, as 5% solutions in chloroform using a 0.1 mm. liquid cell. The chloroform solutions were useful in revealing the characteristic furoxan absorption in the 1475–1410 cm.$^{-1}$ region, particularly when no methyl groups were in the sample to interfere.

Table III lists the compounds investigated and the absorption frequencies found in the regions listed as characteristic of the furoxan group. A complete typical spectrum, that of dibenzoylfuroxan, is given in Fig. 1.

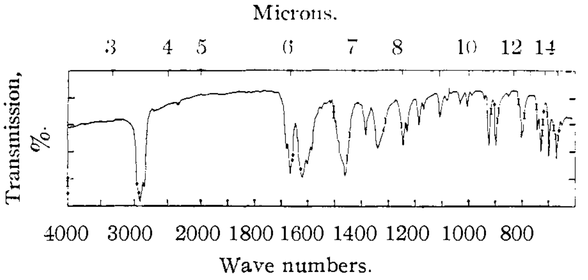


Fig. 1.—The infrared absorption spectrum of dibenzoylfuroxan, in Nujol.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SWARTHMORE COLLEGE]

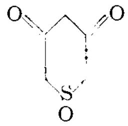
Thiapyran Derivatives. V. The Monosulfinyl and Monosulfonyl Analogs of Phloroglucinol[1]

BY EDWARD A. FEHNEL AND ALBERT P. PAUL

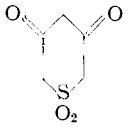
RECEIVED FEBRUARY 11, 1955

Tetrahydrothiapyran-3,5-dione 1-oxide and tetrahydrothiapyran-3,5-dione 1,1-dioxide have been synthesized to test the hypothesis that these compounds might be capable of undergoing a prototropic aromatization analogous to the rearrangement of 1,3,5-cyclohexanetrione to phloroglucinol. A study of the acidity constants and ultraviolet absorption spectra of the products shows that the monoenols and the corresponding enolate anions are the only major species present in aqueous and alcoholic solutions. It is concluded that any conjugative ability possessed by the sulfinyl and sulfonyl functions must be inoperative in these molecules.

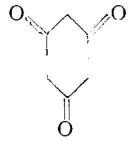
Tetrahydrothiapyran-3,5-dione 1-oxide (I) and tetrahydrothiapyran-3,5-dione 1,1-dioxide (II) may be regarded as the monosulfinyl and monosulfonyl analogs, respectively, of a tricarbonyl compound (1,3,5-cyclohexanetrione, III) which is known to exist predominantly, if not exclusively, in the trienolic form (phloroglucinol, IV). In view of recent results[2] attesting to the conjugative ability of the sulfinyl and sulfonyl groups, it seemed of interest to investigate the possibility that I and II might exist in equilibrium with tautomeric forms (V, VI) analogous to IV. The demonstration of the existence of such forms should provide conclusive evidence of the ability of the sulfinyl and sulfonyl functions to interact with adjacent groups by a resonance mechanism.



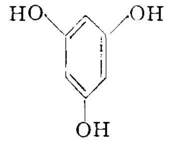
I



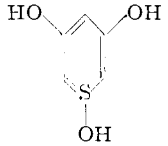
II



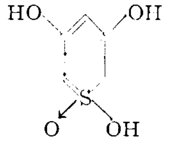
III



IV



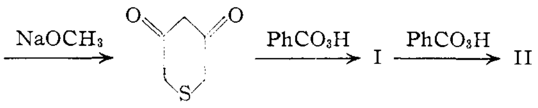
V



VI

To obtain the desired sulfoxide I and sulfone II, tetrahydrothiapyran-3,5-dione (VII) was synthesized and subjected to stepwise oxidation with perbenzoic acid, as shown in the following sequence of reactions

$$CH_3COCH_2Cl + NaSCH_2COOCH_3 \longrightarrow CH_3COCH_2SCH_3COOCH_3$$



VII

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(1) Based on a thesis submitted by Albert P. Paul in partial fulfillment of the requirements for the M.A. degree, Swarthmore College, 1951. Presented before the Division of Organic Chemistry, 126th Meeting of the American Chemical Society, New York, N. Y., 1954. This investigation was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation.

(2) (a) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949); **72**, 1292 (1950); (b) H. P. Koch, *J. Chem. Soc.*, 408 (1949); (c) D. Barnard, J. M. Fabian and H. P. Koch, *ibid.*, 2442 (1949); (d) R. H. Eastman and R. M. Wagner, THIS JOURNAL, **71**, 4089 (1949); (e) H. H. Szmant and H. J. Planinsek, *ibid.*, **72**, 4042 (1950); (f) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); (g) E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, THIS JOURNAL, **73**, 1220 (1951); (h) F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952); (i) H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **71**, 295 (1952); **72**, 655 (1953); (j) E. S. Waight, *J. Chem. Soc.*, 2440 (1952); (k) F. G. Bordwell and P. J. Boutan, Abstracts of the 124th Meeting of the American Chemical Society, 1953, p. 80-O; (l) F. G. Bordwell and H. M. Andersen, THIS JOURNAL, **75**, 6019 (1953).