"Mesoionic" Rhodanine Derivatives

Preparation and Crystal Structure Determination

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The anions of 3-substituted 5-phenylrhodanines are S-alkylated by alkyl halides, and the resulting compounds are formulated as the "mesoionic" anhydro-2-alkylthio-3-R-4-hydroxy-5-phenyl-thiazolium hydroxides. This structure has been conclusively demonstrated by an X-ray analysis. The observed bond lengths show that the compounds are best represented as betaines with the positive charge on the nitrogen atom and the negative charge on the oxygen atom. Some observed deviations from normal bond lengths can be attributed to close intramolecular contacts. The infrared and ultraviolet spectra are discussed in relation to the verified structure.

The term "mesoionic" has been proposed by Baker and Ollis [1] for compounds in which a negative charge is associated with an atom or groups of atoms covalently bonded to a five- or six-membered heteroaromatic ring, which carries a positive charge and for which no single satisfactory covalent or polar structure can be written. The necessity and usefulness of this term has been disputed [2] but it seems to have served some purpose since it has been widely used during the last decade. It has previously been observed [3] that the anion of 3-amino-5-acetyl-rhodanine was alkylated by alkyl halides on the exocyclic sulphur atom, and the resulting products were formulated as mesoionic 3-amino-5-1'-hydroxyethylidene-4-oxothiazolinium hydroxide anhydro salts. In order to obtain simple representatives of this ring system, attempts were made to alkylate the anions of some 5-phenylrhodanines (I) in a similar way. The reaction was found to follow the expected route, and a series of new mesoionic compounds has thus been prepared. The stability of these compounds is never particularly high and depends on the nature of the substituents in the 3-position.

I

a, R = CH₃
b, R = NH₂
c, R = N(CH₃)₂
d, R = N:CHPh

II

a, R = R' = CH₃
b, R = NH₂, R' = CH₃
c, R = NH₂, R' = CH₂Ph
d, R = N:CHPh, R' = CH₃
e, R = N:CHPh, R' = CH₂Ph
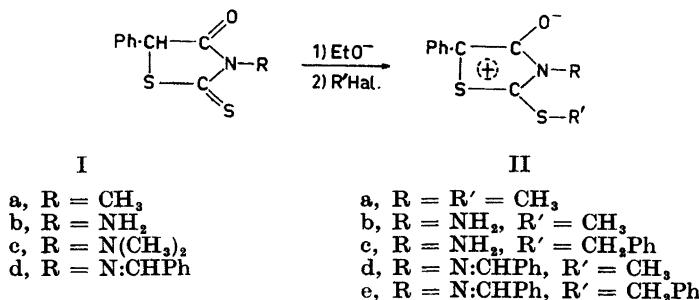
That S-alkylation and not C-alkylation has occurred is shown by the formation of mercaptan on acidic or alkaline decomposition. Attempts to prepare a mesoionic compound with R = N(CH$_3$)$_2$ probably gave the desired product. However, it decomposed too rapidly to be analysed. The greater stability of the otherwise very similar IIb may be due to a hydrogen bond between the amino group and the oxygen atom. The benzylidenamino compounds IId — e may owe their stability to a conjugation effect, which is also obvious in their ultraviolet spectra.

The mesoionic compounds form slightly soluble addition compounds with sodium iodide, which crystallize when the rhodanines are methylated with methyl iodide and sodium ethoxide.

In order to prove that the arrangement of the atoms is as proposed and to provide a basis for a discussion of the electronic structure of the molecule, the compound IIb was subjected to an X-ray structure analysis.

PREPARATIVE PART

3-Methyl-5-phenyl-rhodanine (Ia). Potassium methyldithiocarbamate (72.5 g) was added to a solution of α-bromophenylacetic acid (107.5 g) and sodium hydrogen carbonate (46.5 g) in water (200 ml). After 5 h the separated solid product was filtered, and the filtrate was acidified with hydrochloric acid, which caused a further quantity of less pure product to separate. Recrystallization from absolute ethanol gave colourless needles (47.8 g, 43 % yield), m.p. 86—87°. (Found: C 53.8; H 4.23; N 6.25; S 28.9. C$_{10}$H$_9$NOS$_2$ (223.32) requires C 53.8; H 4.06; N 6.27; S 28.7).

Anhydro-2-methylthio-3-methyl-4-hydroxy-5-phenylthiazolium hydroxide (IIa). Methyl iodide (1.5 g) was added to an ice-cold solution of 3-methyl-5-phenyl-rhodanine (Ia, 2.23 g) in N NaOEt in absolute ethanol (10 ml). On the following day a yellow precipitate had formed (3.47 g, 90 % yield), which consisted of a sodium iodide complex of (IIa). This compound (3.9 g) was dissolved in ethanol (25 ml), and water (10 ml), was added. On evaporation of the ethanol a deep-yellow crystalline precipitate was formed (2.0 g, 84 % yield), which crystallized from toluene as deep-yellow prisms, m.p. 146.5—147°. (Found: C 55.9; H 4.66; N 5.97; S 26.9. C$_{11}$H$_{11}$NOS$_2$ (237.35) requires C 55.7; H 4.67; N 5.90; S 27.0). Addition of nitric acid and silver nitrate solution to the water extract from the crude product gave a 95 % yield of silver iodide.

Anhydro-2-methylthio-3-amino-4-hydroxy-5-phenyl-thiazolium hydroxide (IIb). 3-Amino-5-phenyl-rhodanine [4] (Ib, 5.5 g) and methyl iodide (3.6 g) reacted in N NaOEt (25 ml) to give a sodium iodide complex of (IIb, 7.00 g, 73 % yield), m.p. 214° (decomp.). The product was dissolved in ethanol (400 ml), and the solution was poured into water (500 ml). On cooling to −30° a deep-yellow crystalline product separated (4.60 g, 77 %

yield), m.p. 179—180°. The product crystallized from toluene as long, yellow needles of unchanged m.p. (Found: C 50.1; H 4.20; N 11.8; S 26.9. $C_{10}H_{10}N_2OS_2$ (238.32) requires C 50.4; H 4.23; N 11.8; S 26.9).

Anhydro-2-benzylthio-3-amino-4-hydroxy-5-phenyl-thiazolium hydroxide (IIc). When (Ib, 22.4 g) reacted with benzyl chloride (13 g) in N NaOEt (100 ml), the mesoionic compound separated as deep-yellow prisms (22.5 g, 72 % yield). Recrystallization from toluene gave deep-yellow plates, m.p. 163—164°. (Found: C 62.0; H 4.51; N 8.85; S 20.0. $C_{16}H_{14}N_2OS_2$ (314.44) requires C 61.6; H 4.49; N 8.80; S 20.1).

This compound (1.57 g) was refluxed for 12 h with 10 equiv. of sodium hydroxide in 50 % aqueous ethanol (25 ml). A solution of iodine (1.27 g) in potassium iodide solution was added. A crystalline precipitate was formed (0.37 g, 60 % yield), which crystallized from ethanol as colourless plates, m.p. 69—69.5°, identified by mixed m.p. and infrared spectrum as *dibenzyldisulphide.*

Anhydro-2-methylthio-3-benzylidenamino-4-hydroxy-5-phenyl-thiazolium hydroxide (IId). 3-Benzylidenamino-5-phenyl-rhodanine [4] (3.12 g) and methyl iodide (1.5 g) reacted in cold N NaOEt (10 ml). On the following day a deep-red solid product had formed (1.11 g, 34 % yield), which crystallized from toluene-heptane as deep-red prisms, m.p. 155—156°. (Found: C 62.0; H 4.48; N 8.55; S 19.6. $C_{17}H_{14}N_2OS_2$ (326.45) requires C 62.6; H 4.32; N 8.58; S 19.6).

Anhydro-2-benzylthio-3-benzylidenamino-4-hydroxy-5-phenyl-thiazolium hydroxide (IIe). When benzyl chloride was substituted for methyl iodide in the previous experiment, a 63 % yield of a red, crystalline product was obtained, which crystallized from toluene-heptane as red prisms, m.p. 144—145°. (Found: C 68.4; H 4.68; N 7.06; S 15.9. $C_{23}H_{18}N_2OS_2$ (402.55) requires C 68.6; H 4.51; N 6.96; S 15.9).

3-Dimethylamino-5-phenyl-rhodanine (Ic). N,N-Dimethylhydrazinium 3,3-dimethyl-dithiocarbazate [5] (7.8 g) was added to a solution of α-bromophenylacetic acid (8.6 g) and sodium hydrogen carbonate (3.7 g) in water (100 ml). After 5 h the solution was acidified with hydrochloric acid, and a non-crystallizing product was obtained. Since this was soluble in sodium hydrogen carbonate solution, it was regarded as the intermediate substituted phenylacetic acid. This was dissolved in sodium hydrogen carbonate solution, excess acetic acid was added, and the solution was refluxed for 4 h. After cooling, a solid product was obtained (3.0 g, 30 % yield), which crystallized from absolute ethanol as pale yellow rods, m.p. 154°. (Found: C 52.4; H 4.87; N 11.1; S 25.5. $C_{11}H_{12}N_2OS_2$ (252.37) requires C 52.4; H 4.79; N 11.1; S 25.4). When this rhodanine reacted with methyl iodide in the usual way, no crystalline product separated. The solution was evaporated, and the organic material was extracted with carbon tetrachloride. From this solution a reddish-yellow, crystalline product could be obtained, but it decomposed rapidly to a brown, semisolid mass. Repeated recrystallization gave some crystalline product, but this was equally unstable, and no further attempts were made to isolate the desired mesoionic compound.

X-RAY DATA

IIa is unstable and attempts to collect X-ray data were unsuccessful. Crystals of IIb also deteriorate in the X-ray beam, but it was possible to collect three-dimensional data by using several crystals. They are monoclinic ($P2_1$) with

$$a = 8.84 \pm 0.05 \text{ Å}, b = 5.14 \pm 0.03 \text{ Å}, c = 11.99 \pm 0.06 \text{ Å}$$
$$\beta = 96.23° \pm 0.5°$$

Weissenberg photographs (CuKα radiation) were taken for layers 0—2 about the a and b axes. Intensities were estimated visually and corrected for the Lorentz and polarization factors but not for absorption.

STRUCTURE DETERMINATION

A Patterson series was calculated with coefficients sharpened to correspond to those from point atoms at rest. It was not possible to identify with certainty the S—S vectors and a still sharper series was calculated.[6] The heavy atom vectors were then easily found. The usual heavy atom technique was used to locate the other atoms of the structure. All hydrogen atoms were found from difference maps. They were, however, included in the structure factor computation with their calculated coordinates and with isotropic temperature factors. Their parameters were not varied in the following block diagonal least-squares refinement. Anisotropic temperature factors were used for the other atoms. At an R-value of 11.4 % no further improvement occurred. All shifts were then smaller than 1/3 of the standard deviations.

The least-squares programme minimizes $\sum w\ |F_o - F_c|^2$ where the weight was [7]

$$w = \frac{1}{1 + \left[\dfrac{|F_o| - 2.5\ |F_{min}|}{2.2\ |F_{min}|}\right]^2}$$

The formfactors used are those given in the *International Tables for X-Ray Crystallography*, Vol. III, p. 202. The Datasaab D21 computer was used for the calculation with programmes written by Abrahamsson *et al.*[8]

RESULTS AND DISCUSSION

The final parameters are given in Tables 1—3. Observed and calculated structure factors are listed in Table 4. The atomic numbering is shown in Fig. 1, bond distances and angles in Fig. 2. The latter also appear in Tables 5 and 6 with estimated standard deviations.[9],[10]

Table 1. Fractional coordinates with standard deviations ($\times 10^5$) for the heavier atoms of the molecule.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
S(1)	0.18923	(43)	−0.01085	(116)	0.25653	(34)
S(6)	0.43943	(44)	0.07625	(118)	0.09534	(34)
O(8)	0.06616	(111)	0.02428	(260)	0.89835	(83)
N(3)	0.17711	(128)	0.31219	(339)	0.10067	(108)
N(7)	0.20894	(129)	0.45547	(304)	0.00537	(89)
C(2)	0.27264	(163)	0.15407	(256)	0.14903	(105)
C(4)	0.03013	(146)	0.34519	(353)	0.14627	(120)
C(5)	0.02815	(142)	0.20903	(405)	0.23857	(109)
C(9)	0.49693	(249)	0.32659	(394)	0.80831	(162)
C(10)	0.91028	(141)	0.15674	(361)	0.31779	(141)
C(11)	0.77412	(219)	0.33957	(415)	0.30340	(137)
C(12)	0.66721	(175)	0.30400	(411)	0.37749	(177)
C(13)	0.67390	(197)	0.11616	(464)	0.46540	(186)
C(14)	0.79467	(260)	−0.02256	(678)	0.47017	(171)
C(15)	0.90805	(187)	−0.03739	(592)	0.39999	(156)

Table 2. Allowance was made for anisotropic vibrations with exp $-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{31} + 2hka^*b^*U_{12})$. The U_{ij}s are given together with standard deviations ($\times 10^4$) within brackets.

	U_{11}		U_{22}		U_{33}		U_{23}		U_{13}		U_{12}	
S(1)	0.0458	(20)	0.0393	(27)	0.0500	(22)	0.0003	(24)	0.0089	(17)	0.0137	(29)
S(6)	0.0439	(19)	0.0432	(28)	0.0577	(24)	−0.0053	(27)	0.0135	(18)	0.0167	(31)
O(8)	0.0491	(54)	0.0430	(88)	0.0580	(64)	−0.0156	(71)	0.0068	(48)	−0.0197	(83)
N(3)	0.0352	(63)	0.0384	(88)	0.0593	(82)	0.0077	(81)	0.0101	(58)	−0.0025	(86)
N(7)	0.0387	(57)	0.0337	(74)	0.0343	(61)	0.0045	(75)	0.0034	(51)	−0.0100	(81)
C(2)	0.0486	(72)	−0.0026	(64)	0.0284	(65)	0.0041	(61)	0.0166	(59)	0.0272	(85)
C(4)	0.0283	(68)	0.0352	(99)	0.0493	(94)	−0.0519	(95)	−0.0149	(64)	0.0110	(96)
C(5)	0.0282	(66)	0.0616	(125)	0.0266	(73)	0.0254	(91)	−0.0123	(58)	0.0362	(97)
C(9)	0.1479	(185)	0.0398	(109)	0.0953	(139)	−0.0479	(126)	0.0838	(135)	−0.1349	(170)
C(10)	0.0208	(66)	0.0244	(94)	0.0900	(123)	0.0121	(100)	0.0141	(74)	−0.0166	(92)
C(11)	0.0928	(128)	0.0345	(98)	0.0601	(111)	−0.0213	(109)	0.0492	(103)	0.0016	(139)
C(12)	0.0362	(79)	0.0428	(125)	0.1152	(154)	0.0456	(127)	0.0145	(90)	−0.0131	(118)
C(13)	0.0594	(107)	0.0493	(146)	0.1366	(180)	0.0243	(159)	0.0446	(115)	0.0349	(140)
C(14)	0.1093	(156)	0.1704	(317)	0.0827	(143)	0.0636	(211)	0.0343	(121)	−0.0872	(210)
C(15)	0.0514	(91)	0.1026	(189)	0.0786	(117)	−0.0026	(156)	0.0236	(87)	0.0225	(143)

Table 4. Observed and calculated structure factors ($\times 100$). Fi is the phase angle in fractions of a revolution.

h	k	l	Fobs	Fcalc	Fi
0	0	2	992	1350	0.5000
0	0	3	1763	1655	0.5000
0	0	4	602	581	0.5000
0	0	5	2289	2827	0.5000
0	0	6	2109	2327	0.5000
0	0	7	564	532	1.0000
0	0	8	1648	1935	1.0000
0	0	9	712	776	1.0000
0	0	10	417	388	1.0000
0	0	11	742	799	1.0000
0	0	12	751	1007	1.0000
1	0	1	2122	2591	0.5000
1	0	2	6365	7014	0.5000
1	0	3	2912	2607	0.5000
1	0	4	549	472	1.0000
1	0	5	894	901	1.0000
1	0	7	2316	2834	1.0000
1	0	-2	2775	3530	0.5000
1	0	-3	618	520	0.5000
1	0	-4	1524	1740	1.0000
1	0	-5	1009	1067	1.0000
1	0	-7	706	852	0.5000
1	0	-8	1172	1421	1.0000
1	0	-9	840	987	1.0000
1	0	-10	713	833	0.5000
1	0	-11	1217	1560	0.5000
1	0	-12	655	684	1.0000
1	0	-13	524	657	1.0000
2	0	0	593	839	0.5000
2	0	1	1181	1667	1.0000
2	0	2	709	583	1.0000
2	0	3	1275	1171	1.0000
2	0	4	1718	1887	0.5000
2	0	5	1659	1689	0.5000
2	0	6	1295	1458	0.5000
2	0	7	794	862	0.5000
2	0	8	1153	1338	0.5000
2	0	-1	2158	2563	0.5000
2	0	-2	1348	1790	0.5000
2	0	-3	4828	4938	0.5000
2	0	-4	5478	4941	0.5000
2	0	-5	946	959	0.5000
2	0	-6	327	443	0.5000
2	0	-7	1799	1927	0.5000
2	0	-8	298	79	0.5001
2	0	-9	1937	2127	1.0000
2	0	-10	640	742	1.0000
2	0	-11	632	629	0.5000
3	0	0	2079	2668	0.5000
3	0	1	785	902	0.5000
3	0	2	752	533	0.5000
3	0	3	1595	1456	0.5000
3	0	4	1924	1828	0.5000
3	0	5	712	703	1.0000
3	0	6	1075	1377	1.0000
3	0	8	566	465	1.0000
3	0	-1	2083	2608	0.5000
3	0	-2	202	2269	1.0000
3	0	-3	178	190	0.5000
3	0	-4	1022	1348	0.5000
3	0	-5	1751	1717	1.0000
3	0	-6	761	844	1.0000
3	0	-8	1515	1588	0.5000
3	0	-9	862	1032	0.5000
3	0	-10	735	823	0.5000
3	0	-11	512	578	0.5000
3	0	-12	446	442	0.5000
3	0	-13	361	366	1.0000
4	0	0	1142	1399	1.0000
4	0	1	4581	4590	1.0000
4	0	2	457	383	1.0000
4	0	3	790	1055	1.0000
4	0	4	2317	2541	1.0000
4	0	5	1438	1426	1.0000
4	0	7	1095	1461	1.0000
4	0	8	379	464	0.5000
4	0	-1	1487	2066	0.5000
4	0	-2	2412	2080	0.5000
4	0	-3	3646	3125	0.5000
4	0	-4	1200	1200	0.5000
4	0	-5	1256	1334	0.5000
4	0	-6	1365	1537	0.5000
4	0	-7	3051	3347	0.5000
4	0	-8	1328	1321	1.0000
5	0	0	1955	1812	1.0000
5	0	1	884	828	1.0000
5	0	2	1551	1552	0.5000
5	0	3	947	1004	0.5000
5	0	4	1819	1984	0.5000
5	0	6	867	909	0.5000
5	0	8	847	1143	1.0000
5	0	-1	1785	1742	1.0000
5	0	-2	571	394	1.0000
5	0	-3	1601	1426	1.0000
5	0	-4	1621	1432	1.0000
5	0	-5	1161	1274	0.5000
5	0	-6	1061	1205	0.5000
5	0	-8	711	789	1.0000
5	0	-9	455	505	1.0000
5	0	-10	532	429	0.5000
5	0	-11	430	398	1.0000
5	0	-12	405	487	1.0000
6	0	0	297	43	0.9999
6	0	1	1429	1329	0.5000
6	0	3	1335	1437	1.0000
6	0	4	1475	1605	0.5000
6	0	6	424	501	0.5000
6	0	-2	1717	1620	0.5000
6	0	-3	2645	2235	0.5000
6	0	-4	873	905	1.0000
6	0	-5	1479	1697	1.0000
6	0	-6	450	399	1.0000
6	0	-8	1140	1356	1.0000
6	0	-9	592	680	1.0000
6	0	-10	582	665	1.0000
6	0	-11	415	270	0.5000
7	0	0	800	588	1.0000
7	0	1	1007	1003	0.5000
7	0	4	1043	1225	0.5000
7	0	5	788	992	0.5000
7	0	7	530	502	0.5000
7	0	-1	2579	2466	1.0000
7	0	-2	1126	1009	1.0000
7	0	-5	1315	1446	0.5000
7	0	-6	780	861	1.0000
7	0	-7	1382	1615	1.0000
8	0	0	2071	2097	0.5000
8	0	1	1733	1723	0.5000
8	0	5	787	1000	1.0000
8	0	6	807	1021	1.0000
8	0	-1	455	380	1.0000
8	0	-2	385	263	1.0000
8	0	-3	298	334	1.0000
8	0	-5	723	863	1.0000
8	0	-6	908	1057	1.0000
8	0	-7	401	334	1.0000
8	0	-8	661	707	0.5000
8	0	-9	324	456	0.5000
9	0	0	368	517	1.0000
9	0	-2	369	309	1.0000
9	0	-3	744	774	1.0000
9	0	-4	471	495	0.5000
9	0	-5	621	827	0.5000
9	0	-7	350	330	1.0000
10	0	0	311	151	1.0000
10	0	1	469	422	0.5000
10	0	2	526	627	0.5000
10	0	-2	488	314	0.5000
10	0	-3	564	673	1.0000
10	0	-4	632	945	1.0000
0	1	1	5437	5858	0.3758
0	1	2	858	1046	0.5931
0	1	3	1805	2058	0.5910
0	1	4	1629	1771	0.5486
0	1	5	2225	2434	0.2057
0	1	6	1769	1414	0.9353
0	1	7	1358	1387	0.8272
0	1	8	646	609	0.8863
0	1	9	591	463	0.3043
0	1	10	733	660	0.7112
0	1	11	375	652	0.7860
1	1	0	1162	1315	0.3116
1	1	1	3981	5196	0.4855
1	1	2	7314	9476	0.7216
1	1	3	4533	5106	0.8862
1	1	4	1888	2206	0.8836
1	1	5	780	899	0.8224
1	1	6	1178	1077	0.7982
1	1	7	724	1017	0.4054
1	1	-1	2797	2555	0.3421
1	1	-2	400	236	0.3994
1	1	-3	3118	3155	0.2772
1	1	-4	1044	1093	0.2058
1	1	-5	2379	2205	0.7303
1	1	-6	2929	3592	0.7837
1	1	-7	835	803	0.8491
1	1	-8	546	639	0.7306
1	1	-9	1173	1375	0.7432
1	1	-10	741	779	0.8335
1	1	-11	650	725	0.3427
1	1	-12	975	981	0.3373
2	1	0	1337	1460	0.5925
2	1	1	1561	1581	0.8708
2	1	2	2340	2685	0.6572
2	1	3	1260	1247	0.0906
2	1	4	2415	2933	0.2635
2	1	5	1157	1404	0.5678
2	1	6	414	204	0.2297
2	1	7	724	680	0.0824
2	1	-1	237	110	0.7176
2	1	-2	2339	2493	0.7055
2	1	-3	1904	1893	0.7793
2	1	-4	1398	1419	0.1624
2	1	-5	702	507	0.2341
2	1	-6	1568	1523	0.7921
2	1	-7	609	620	0.5165
2	1	-8	1105	1248	0.3786
2	1	-9	961	1152	0.2197
2	1	-10	1005	1277	0.7788
2	1	-11	1415	1025	0.3664
3	1	0	1707	1378	0.4674
3	1	1	2368	2371	0.2000
3	1	3	1186	1559	0.0428
3	1	4	2104	2063	0.8853
3	1	5	1952	2043	0.7895
3	1	-1	3962	5220	0.2196
3	1	-2	3623	3898	0.2792
3	1	-3	1558	1420	0.6672
3	1	-4	1806	1983	0.5558
3	1	-5	883	711	0.9066
3	1	-6	2088	1870	0.9118
3	1	-7	2254	2508	0.8040
3	1	-8	485	427	0.0352
3	1	-9	1663	1790	0.1910
3	1	-10	649	800	0.3807
3	1	-11	645	697	0.3640
3	1	-12	498	590	0.3452
3	1	-13	443	456	0.2968
4	1	0	2368	2338	0.8399
4	1	1	745	627	0.3523
4	1	2	2433	2446	0.2023
4	1	3	761	923	0.9516
4	1	4	849	626	0.6685
4	1	5	1245	1327	0.3453
4	1	6	1526	1591	0.2608
4	1	8	745	729	0.6489
4	1	-1	730	692	0.0798
4	1	-2	2343	2410	0.0825
4	1	-3	374	277	0.8761
4	1	-4	1143	862	0.4922
4	1	-5	1320	1506	0.3480
4	1	-6	2125	2217	0.3495
4	1	-7	799	855	0.4882
4	1	-9	878	983	0.0215
4	1	-10	888	928	0.0930
4	1	-11	365	420	0.9585
4	1	-12	567	650	0.6478
5	1	0	1681	1750	0.3980
5	1	1	2241	2239	0.3077
5	1	2	1368	1536	0.3255
5	1	3	1359	1476	0.7954
5	1	4	944	811	0.8093
5	1	6	830	859	0.8092
5	1	7	1332	1495	0.7895
5	1	8	530	587	0.6553
5	1	9	726	731	0.2646
5	1	-1	654	481	0.3401
5	1	-2	1101	988	0.0546
5	1	-3	504	462	0.0542
5	1	-4	1764	1948	0.7918
5	1	-5	2749	3124	0.7550
5	1	-6	664	718	0.9102
5	1	-7	939	851	0.2998
5	1	-8	619	835	0.4285
5	1	-9	375	482	0.5128
5	1	-10	876	1152	0.2049
5	1	-11	800	846	0.2281
5	1	-12	447	298	0.7050
6	1	0	331	349	0.5659
6	1	1	765	675	0.7803
6	1	2	1670	1680	0.7689
6	1	3	952	1105	0.7165
6	1	4	513	575	0.2728
6	1	5	742	920	0.3068
6	1	6	531	608	0.6811
6	1	-1	1042	1091	0.7392
6	1	-2	1085	1340	0.7592
6	1	-3	1907	1890	0.1950
6	1	-4	1543	1490	0.3409
6	1	-5	840	793	0.6773
6	1	-6	729	573	0.7759
6	1	-7	645	534	0.5179

h	k	l	Fobs	Fcalc	Fi
6	1	-8	375	315	0.5333
6	1	-9	914	1191	0.7780
6	1	-10	592	425	0.8574
7	1	0	828	1108	0.3702
7	1	1	866	851	0.4905
7	1	2	740	630	0.4066
7	1	3	1261	1327	0.2578
7	1	4	856	878	0.2043
7	1	5	625	586	0.9019
7	1	6	901	995	0.8085
7	1	-2	2340	2380	0.8333
7	1	-3	732	858	0.8569
7	1	-4	523	368	0.7147
7	1	-5	625	760	0.0231
7	1	-6	889	990	0.7913
7	1	-7	528	428	0.3251
7	1	-8	903	1039	0.2489
7	1	-9	493	640	0.3828
8	1	0	628	926	0.4416
8	1	1	750	940	0.8049
8	1	2	527	669	0.0287
8	1	3	521	823	0.1022
8	1	-1	628	674	0.2989
8	1	-2	375	377	0.1720
8	1	-3	750	538	0.5368
8	1	-4	748	706	0.2296
8	1	-5	1001	1192	0.2222
8	1	-7	498	604	0.7836
0	2	2	1071	1237	0.0873
0	2	3	1263	1238	0.0983
0	2	4	1133	1172	0.8159
0	2	5	1550	1640	0.9327
0	-2	5	2137	1936	0.6617
0	2	6	2249	2067	0.5346
0	2	8	1337	1333	0.5666
0	2	9	701	566	0.1232
0	2	11	704	763	0.0067
1	2	0	1287	1658	0.7974
1	2	-1	1123	1224	0.9330
1	2	-2	1547	1934	0.6478
1	2	-3	1789	2233	0.4065
1	2	-4	1848	1763	0.1023
1	2	1	2499	2801	0.6327
1	2	2	1577	1992	0.8203
1	2	3	2096	2074	0.0432
1	2	4	1410	1332	0.3440
1	2	5	1947	1707	0.2814
1	2	6	656	560	0.2627
1	2	7	1056	992	0.9587
1	2	8	777	634	0.7270
1	2	9	966	859	0.4771
2	2	0	1321	1584	0.3346
2	2	-1	1047	1118	0.8324
2	2	-2	1174	1280	0.8019
2	2	-3	3242	3143	0.4580
2	2	-4	3212	3748	0.5455
2	2	-5	838	1104	0.6260
2	2	1	2602	2700	0.2171
2	2	2	3032	3250	0.0988
2	2	3	3039	3480	0.1180
2	2	4	2715	2791	0.4360
2	2	5	2913	2424	0.6007
2	2	6	1814	1568	0.7238
2	2	7	1601	1591	0.6380
2	2	8	1461	1486	0.5285
2	2	9	691	657	0.3346
2	2	10	974	1101	0.1191
2	2	11	654	611	0.1459
3	2	0	2203	2620	0.4093
3	2	-1	819	961	0.6099
3	2	-2	1531	1722	0.0495
3	2	-3	628	772	0.1485
3	2	-4	2104	1857	0.3833
3	2	-5	1145	1403	0.3585
3	2	-6	912	896	0.2136
3	2	1	1394	1291	0.0161
3	2	2	1137	1121	0.8789

h	k	l	Fobs	Fcalc	Fi
3	2	3	1805	1730	0.6203
3	2	4	2010	2033	0.4150
3	2	5	785	603	0.7955
3	2	6	1041	994	0.9259
3	2	7	1063	1006	0.3819
3	2	8	935	1086	0.3596
3	2	9	693	941	0.1322
3	2	10	673	728	0.0433
4	2	0	421	416	0.5341
4	2	-1	1995	2261	0.5658
4	2	-2	819	807	0.6091
4	2	-3	1407	1702	0.8586
4	2	-4	1082	1159	0.6906
4	2	-5	1325	1420	0.5107
4	2	-6	878	853	0.0446
4	2	-7	1618	1744	0.9559
4	2	1	2085	2116	0.0696
4	2	2	1464	1639	0.0830
4	2	3	559	462	0.2211
4	2	4	838	767	0.0651
4	2	5	887	1050	0.9922
4	2	6	1109	1290	0.7132
4	2	7	1011	1263	0.5312
4	2	9	575	668	0.9153
5	2	0	1297	1700	0.9209
5	2	-1	1006	1145	0.3592
5	2	-2	791	971	0.3044
5	2	-3	959	1058	0.0241
5	2	-4	1789	2042	0.0254
5	2	-5	901	1187	0.2769
5	2	-6	1111	1198	0.6804
5	2	-7	1102	1262	0.7819
5	2	1	984	1241	0.8733
5	2	2	1318	1435	0.6445
5	2	3	746	686	0.6404
5	2	4	775	681	0.9205
6	2	0	1129	1538	0.6656
6	2	-1	1214	1443	0.7075
6	2	-2	1391	1624	0.6188
6	2	-3	891	970	0.6265
6	2	-4	1118	1519	0.0827
6	2	-5	925	1004	0.1927
6	2	-6	583	688	0.0829
6	2	-7	694	870	0.1515
6	2	-8	820	969	0.0211
6	2	1	888	825	0.4832
6	2	2	1113	1438	0.2863
6	2	3	1478	1632	0.1174
6	2	4	1447	1531	0.0978
7	2	0	823	995	0.3412
7	2	-1	687	705	0.1542
7	2	-2	582	494	0.5028
7	2	-4	586	559	0.5086
7	2	-5	586	502	0.0579
7	2	-8	648	616	0.6730
7	2	1	691	716	0.2865
7	2	2	586	657	0.1154
7	2	4	688	736	0.5875
7	2	5	673	584	0.5501
8	2	0	1105	1206	0.5472
8	2	-1	820	975	0.5821
8	2	-2	685	704	0.8570
8	2	-4	571	777	0.4232
8	2	-5	663	742	0.1000
8	2	-6	768	646	0.0254
0	3	1	863	1002	0.2624
0	3	2	1582	1533	0.5897
0	3	3	931	1477	0.5682
0	3	4	570	643	0.3974
0	3	5	664	875	0.2098
0	3	6	626	880	0.8923
0	3	7	787	1175	0.7535
0	3	8	470	562	0.1541
0	3	9	663	733	0.1235
0	4	0	655	1012	0.2275
0	4	1	657	770	0.2522
0	4	2	637	781	0.4027

h	k	l	Fobs	Fcalc	Fi
0	4	3	530	899	0.8666
0	4	4	1405	1912	0.8501
0	4	5	804	1083	0.8006
0	4	6	745	1022	0.5916
0	4	7	658	558	0.6887
0	5	1	503	819	0.0490
0	5	2	597	437	0.7245
0	5	3	1023	1484	0.7349
0	5	4	518	455	0.6952
0	5	5	501	641	0.3876
1	3	0	1505	1136	0.3481
1	3	1	876	795	0.1630
1	3	2	1133	1036	0.8845
1	3	4	1210	1213	0.8768
1	3	5	900	1052	0.9904
1	3	6	996	1060	0.7865
1	3	6	1310	1704	0.6854
1	3	7	839	874	0.5337
1	3	8	1228	1319	0.3489
1	3	9	697	806	0.4048
1	3	-1	1965	2033	0.5130
1	3	-2	1846	2317	0.6029
1	3	-3	1465	1466	0.4753
1	3	-4	1580	1631	0.2190
1	3	-5	1308	1232	0.6540
1	3	-6	1421	1534	0.7654
1	3	-7	905	995	0.8960
1	4	0	1318	1530	0.8535
1	4	1	579	499	0.4758
1	4	2	943	732	0.9116
1	4	3	1225	1269	0.9082
1	4	4	777	394	0.8463
1	4	5	1181	1222	0.4958
1	4	6	1072	1050	0.3875
1	4	7	773	665	0.2713
1	4	-1	1321	1233	0.9369
1	4	-2	969	790	0.3899
1	4	-3	1422	1451	0.4594
1	4	-4	774	664	0.0605
1	4	-5	1069	1117	0.0422
1	4	-6	1020	1126	0.4212
1	4	-7	603	804	0.4359
1	5	0	695	715	0.2768
1	5	1	842	986	0.9975
1	5	3	589	571	0.4511
1	5	-1	969	1049	0.6268
1	5	-2	1108	1177	0.5866
1	5	-3	829	983	0.5014
1	5	-4	670	551	0.4514
2	3	0	1732	1813	0.1714
2	3	1	1269	1361	0.8065
2	3	2	1380	1517	0.5705
2	3	4	1737	1491	0.3585
2	3	5	1189	1269	0.6174
2	3	6	1903	1914	0.7119
2	3	7	896	899	0.6590
2	3	8	984	947	0.2764
2	3	-1	996	1166	0.1817
2	3	-1	2898	2387	0.1566
2	3	-2	1989	1656	0.7368
2	3	-3	1744	1427	0.8647
2	3	-4	631	601	0.1546
2	3	-5	954	1058	0.3953
2	3	-6	1518	1283	0.6018
2	3	-7	1270	1172	0.5704
2	4	1	1179	1275	0.3408
2	4	1	1482	1499	0.3380
2	4	2	1154	1279	0.1352
2	4	3	918	1022	0.8350
2	4	-1	745	1089	0.4637
2	4	-1	999	1085	0.1971
2	4	-2	643	523	0.7934
2	4	-3	1311	1380	0.5859
2	4	-4	661	809	0.7580
2	4	-5	812	758	0.8893
2	4	-7	806	842	0.2609
2	4	-8	778	622	0.3252

Table 3. Fractional coordinates and isotropic temperature factors for the hydrogen atoms.

	x	y	z	B (Å²)
H(91)	0.4190	−0.3292	0.1926	3.70
H(92)	0.5169	−0.0900	0.2803	3.70
H(93)	0.6116	−0.2516	0.1764	3.70
H(74)	0.2303	0.3217	−0.0618	2.20
H(75)	0.3092	0.5763	0.0270	2.20
H(111)	0.7620	0.4892	0.2386	4.70
H(121)	0.5681	0.4315	0.3680	4.70
H(131)	0.5863	0.0933	0.5220	4.70
H(141)	0.8107	−0.1519	0.5426	4.00
H(151)	0.9923	−0.1930	0.4080	4.60

Table 5. Bond distances with standard deviations.

Bond	Length	σ
S(1)—C(5)	1.812 Å	0.017 Å
—C(2)	1.768	0.014
S(6)—C(2)	1.719	0.015
—C(9)	1.776	0.020
O(8)—C(4)	1.326	0.019
N(3)—N(7)	1.412	0.019
—C(2)	1.266	0.019
—C(4)	1.473	0.019
C(5)—C(4)	1.310	0.022
—C(10)	1.508	0.021
C(10)—C(11)	1.522	0.025
—C(15)	1.404	0.031
C(11)—C(12)	1.377	0.027
C(12)—C(13)	1.425	0.031
C(13)—C(14)	1.280	0.034
C(14)—C(15)	1.379	0.030

Table 6. Bond angles with standard deviations.

Angle	θ	σ
C(5) —S(1) —C(2)	89.9°	0.7°
C(2) —S(6) —C(9)	98.6	0.9
C(2) —N(3) —N(7)	121.5	1.2
—C(4)	118.4	1.4
N(7) —N(3) —C(4)	120.1	1.3
S(1) —C(2) —S(6)	127.1	0.8
—N(3)	109.3	1.1
S(6) —C(2) —N(3)	122.3	1.1
O(8) —C(4) —N(3)	118.9	1.4
—C(5)	130.1	1.4
N(3) —C(4) —C(5)	110.2	1.3
S(1) —C(5) —C(4)	110.6	1.1
—C(10)	113.7	1.2
C(4) —C(5) —C(10)	134.4	1.4
C(11)—C(10)—C(5)	114.3	1.5
—C(15)	116.6	1.5
C(5) —C(10) —C(15)	129.2	1.5
C(10)—C(11)—C(12)	115.8	1.6
C(11)—C(12)—C(13)	126.2	1.7
C(12)—C(13)—C(14)	112.2	2.0
C(13)—C(14)—C(15)	131.4	2.5
C(14)—C(15)—C(10)	117.1	2.3

Bond distances and angles. The results of the X-ray analysis confirm the proposed structure. If the electron distribution in the mesoionic molecule is to be described by a qualitative resonance picture, the limiting structures III—V with the excess negative charge on the oxygen atom will probably be the most important ones.

This conclusion is supported by the short C4—C5 distance, which must be essentially a double bond, and by the C4—O8 bond of 1.33 Å. It can be compared with the length of other carbonyl bonds, which are in the range
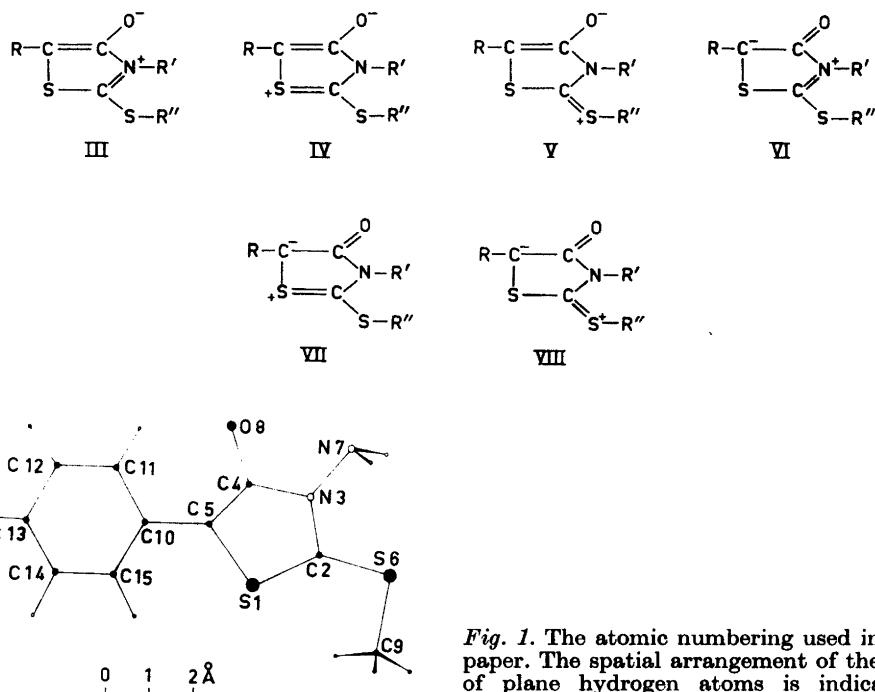
Fig. 1. The atomic numbering used in the paper. The spatial arrangement of the out of plane hydrogen atoms is indicated.
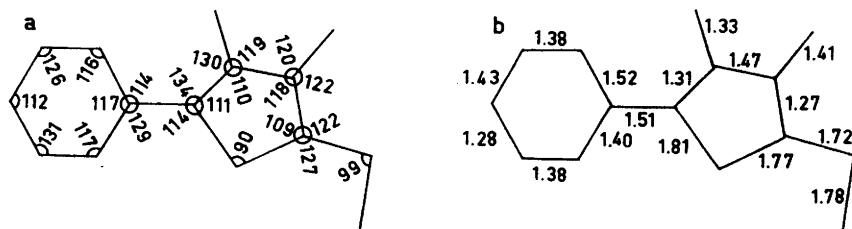
Fig. 2. Bond distances and angles.

1.20—1.22 Å in simple carbonyl compounds and 1.21—1.27 Å in amides. Even in 2-pyridone, in which the polar structure X can be expected to be quite important, the carbonyl bond is only 1.27 Å.[11]
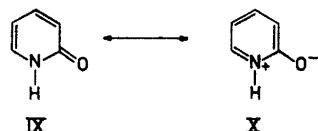
It is interesting to compare the carbonyl bond length in the present compound with that in the sydnone,[12] which is found to be 1.20 Å. This is rather surprising in view of the fact that polar structures like XI and XII are supposed to be important.[13]
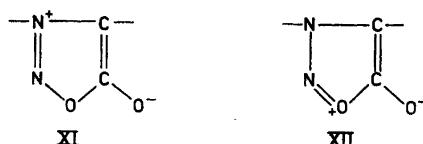
In IIb the C2—N3 bond is quite short, 1.27 Å, compared with 1.37 Å in rhodanine,[14] and must be close to a double bond. The carbon-nitrogen bond in oximes is 1.27 Å.[15] On the other hand, the N3—C4 bond of 1.47 Å is essentially single. Therefore the limiting structure III must have the highest weight. This is in agreement with the rather long carbon-sulphur bonds. The relation between C2—S1 and C2—S6 bonds indicates that the structure V has somewhat higher weight than IV. The C5—S bond, 1.81 Å, is similar to that in rhodanine.[14]

In dithiolium and 1,2,4-dithiazole systems C—S bond lengths range from 1.67 to 1.74 Å [16],[17] and for thiophene a value of 1.718 Å has been found.[18]

Table 7. Least-squares plane through the molecule.

Equation of plane (referred to the crystal axes).	Out of plane deviations (Å)	
0.41235X + 0.42429Y	S(1)	−0.050
+ 0.80619Z − 0.28630 = 0	S(6)	0.034
	O(8)	−0.077
	N(5)	0.003
	N(7)	−0.021
	C(5)	0.049
	C(2)	0.100
	C(4)	−0.080
	C(9)	0.018
	C(10)	−0.005
	C(11)	0.077
	C(12)	0.082
	C(13)	0.031
	C(14)	−0.013
	C(15)	−0.147

The whole molecule is nearly planar. The deviations from the best least-squares plane are given in Table 7. C15 shows the largest deviation. This is no doubt due to strain caused by the close approach to S1 (3.17 Å). The O8—C11 distance is also short (3.08 Å) which results in an opening of the O8—C4—C5 angle (130°) and a displacement of C11 and O1 towards opposite sides of the plane of the molecule. These distortions in the benzene ring might
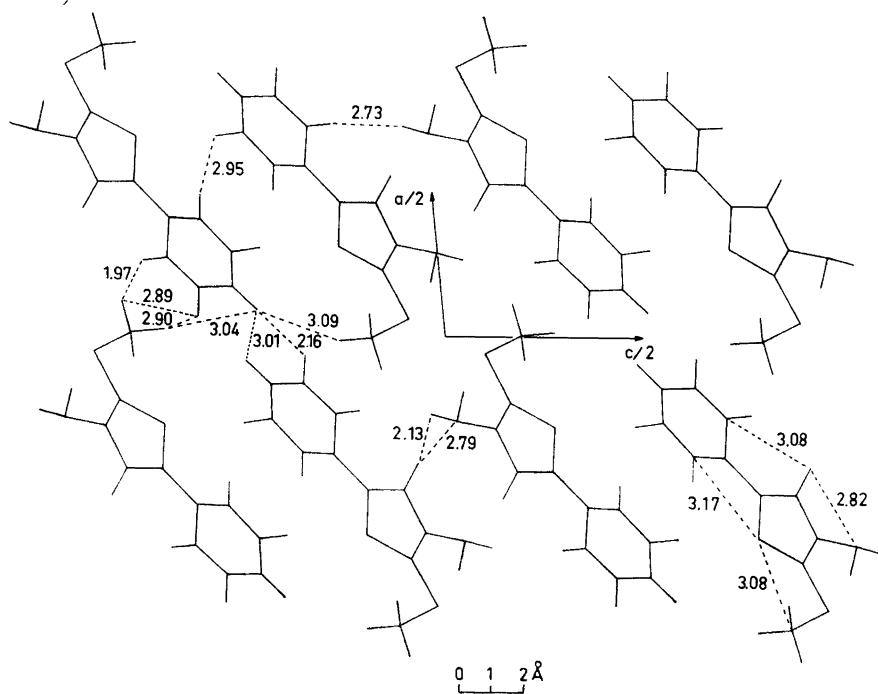
Fig. 3. Molecular packing. Some short intra- and intermolecular contacts are given to the right and left, respectively. Dashed lines represent contacts between one molecule and a *b*-translated equivalent. In this connection it should be pointed out that calculated coordinates have been used for the hydrogen atoms.

explain the abnormal C10—C11 and C13—C14 distances. Another short intramolecular contact is found between S1 and C9 (3.08 Å). Again this is manifested in the opening of the S1—C2—S6 and C2—S6—C9 angles.

The molecular packing is illustrated in Fig. 3. The plane of the molecule forms an angle of 45° with the *ac* plane. The benzene rings thus pack with perpendicular planes about twofold screw axes. Benzene rings are also in contact with the methyl groups. There is a short intermolecular contact (2.79 Å) between O8 and N7 about a screw axis, which no doubt represents a hydrogen bond. The molecules are thus linked together by hydrogen bonds to infinite spirals along the *b*-axis. This is also consistent with *b* being the needle direction of the crystals.

MO-calculations and dipole moment. A molecular orbital calculation with a modified ω-method [19] has been performed. The starting parameters are found in Table 8. In the starting system each carbon atom and the oxygen atom was supposed to supply one π electron and the other heteroatoms two each. The results of this calculation are found in Fig. 4. It appears that the calculation, as usual, exaggerates the smoothing out of the π-binding, but that the bond

Table 8. Atom and bond parameters.

$\alpha_C = \alpha$	$\beta_{CC} = 0.9\beta$
$\alpha_O = \alpha + \beta$	$\beta_{CN} = 0.8\beta$
$\alpha_N = \alpha + 1.5\beta$	$\beta_{CO} = 0.8\beta$
$\alpha_S = \alpha + \beta$	$\beta_{CS} = 0.6\beta$

orders, with the exception of the S1—C2 bond, fall in an order which is qualitatively consistent with the bond lengths. The dipole moment for IIa in benzene solution was found to be 5.21 D. Since the moment for rhodanine is 2.22 D [20] a considerable charge transport must have occurred on the formation of the mesoionic structure. However, the π electron moment of structure III should be about 12 D. A similar discrepancy (12 D to 5.5 D) has been found for the sydnones. Hill and Sutton [21,22] have given strong arguments for back-polarization in the σ-bonds being an important factor in diminishing the total moment in structures with large separated charges. The present work supports this theory, since the bond lengths show the dominant importance of structure III, which certainly should give a higher moment than 5.21 D.

The molecular orbital calculation mentioned above gives a π electron moment of 15.3 D. Changing the parameter ω from 1.0 to 1.4 generally tends to diminish the calculated charge separation, but in the present case the moment is only lowered to 14.7 D. However, it follows from the discussion above that the exaggeration may not be excessively large. The calculated moment direction is from S1 into the ring forming an angle of 14.5° with the S1—C5 bond.

IR and UV spectra. The low bond order (and great length) of the carbonyl bond should be reflected in its stretching vibration in the infrared. For the simple rhodanines $\nu_{C=O}$ is found in the region 1725—1730 cm^{-1}, and in the mesoionic compounds IIa and IIb it is lowered to 1685 cm^{-1} (Table 9). The 3-benzylidenamino-rhodanine Id has $\nu_{C=O} = 1715$ cm^{-1}, and the corresponding mesoionic compound IId 1625 cm^{-1}. In the sodium iodide complex
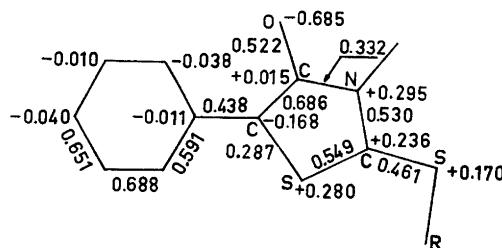

Fig. 4. Net charges and bond orders obtained from MO-calculation ($\omega = 1.0$).

Table 9. Infrared carbonyl stretching frequencies of rhodanines and mesoionic compounds.

Compound	Phase	$\nu_{C=O}$ cm^{-1}
Ia	CCl$_4$	1730
	KBr	1725
IIa	KBr	1685
IIa + NaI	KBr	1605
Id	KBr	1715
IId	KBr	1625
IIe	KBr	1620

of IIa $\nu_{C=O}$ is 1605 cm^{-1}, possibly indicating a coordination of the carbonyl oxygen with the sodium ion.

For the rather similar anhydro-2-phenyl-3-methyl-4-acetyl-5-hydroxy-thiazolinium hydroxide Lawson and Searle[23] report $\nu_{C=O}$ = 1644 cm^{-1} compared to about 1730 for five-membered thiolactones. In contrast to these mesoionic compounds, but in agreement with the short carbonyl bond the N-alkylsydnones have the same carbonyl stretching frequency, 1770 cm^{-1}, as simple γ-lactones. The N-arylsydnones have $\nu_{C=O}$ = 1750 cm^{-1}.[24]

The ultraviolet spectra of all the rhodanines I are rather similar to those of simple N-acylthioamides, with moderate hypsochromic shifts caused by the inclusion in a five-membered ring.[25] This shows that the conjugation between the benzylidenamino group and the ring in Id is quite weak. The formation of the mesoionic system is accompanied by bathochromic shifts (Table 10) of about 100 nm in IIa-c and about 150 nm in IId and IIe. In these mesoionic compounds the conjugation between the benzylidenamino group and the ring is evidently quite considerable. Even in sodium ethoxide solution the rhodanines show substantial bathochromic shifts, showing that a significant electron delocalization occurs also in the anions.

Table 10. Ultraviolet spectra of rhodanines and mesoionic compounds.

Compound	Solvent	λ_{max} nm	ε	λ_{max} nm	ε	λ_{max} nm	ε
Ia	Ethanol	384	71.5	297	16900	262	13000
	NaOEt in ethanol	394.5	15600	301	8600	246.5	9700
IIa	Ethanol	410	a	287.5	a	240.5	a
Ib	Ethanol	370[b]	100	296	18800	—	—
	NaOEt in ethanol	383	17400	299	6600	264	8900
IIb	Ethanol	398.5[c]	12400	276	9600	245.5	9900
IIc	Ethanol	410[c]	12600	274.5	9800	247	9900
Id	Ethanol	393.5	96	291.5	19900	258.5	15600
	NaOEt in ethanol	368	12200	264	14400	249.5	14000
IId	Ethanol	453	6300	275.5	25600	—	—
IIe	Ethanol	458	6400	271.5	22000	—	—

[a] Rapid decomposition. [b] Shoulder. [c] Broad band.

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