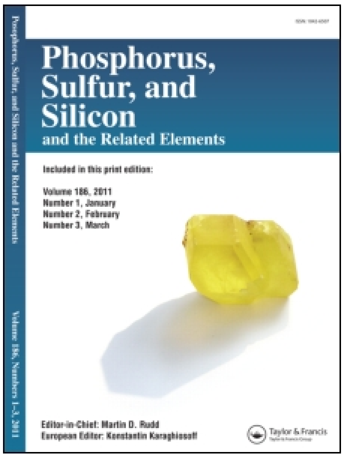


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHYSICOCHEMICAL PROPERTIES AND STRUCTURAL STUDY OF 1,2-DITHIOLYLIUM-4-OLATES AND ISOTHIAZOLIUM-4-OLATES

Daniel Barillier[a]
[a] Laboratoire des Composés Thioorganiques, Université de Caen, Caen Cedex, France

To cite this Article Barillier, Daniel(1980) 'PHYSICOCHEMICAL PROPERTIES AND STRUCTURAL STUDY OF 1,2-DITHIOLYLIUM-4-OLATES AND ISOTHIAZOLIUM-4-OLATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 8: 1, 79 — 85

To link to this Article: DOI: 10.1080/03086648008078165

URL: http://dx.doi.org/10.1080/03086648008078165

Phosphorus and Sulfur, 1980, Vol. 8, pp. 79–86
0308-664X/80/0801-0079$04.50/0

PHYSICOCHEMICAL PROPERTIES AND STRUCTURAL STUDY OF 1,2-DITHIOLYLIUM-4-OLATES AND ISOTHIAZOLIUM-4-OLATES

DANIEL BARILLIER

Laboratoire des Composés Thioorganiques, Université de Caen, 14032, Caen Cedex, France

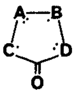
(*Received May 21, 1979; in final form June 29, 1979*)

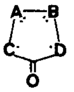
The physicochemical properties of two series of mesoionic compounds, 1,2-dithiolylium-4-olates **3** and isothiazolium-4-olates **4** have been examined.

The negative solvatochromy shown by **3** and **4** in u.v.-vis. is discussed. The unusual i.r. band of **3g** (1488 cm^{-1} in KBr) and **4** (1530 cm^{-1} in KBr) is identified by its large solvent shift. The experimental dipole moments of a few compounds of series **3** and **4** are compared with the theoretical values corresponding to the canonical structures A, B and C. Carbon-13 NMR chemical shift data are given for a number of **3** compounds and compared with data from related 1,2-dithiolylium salts. In connection with the geometry of compound **3a**, determined by X-ray diffraction, the CO group is found to be intermediate between a carbonyl and a single bond C—O.

The discussion deals with the comparison of the CO group in compounds **3** and in tropone **10** or in (4H) thiopyran-4-one **11** and with the comparison of the experimental data with a theoretical electronic structure published by another author.

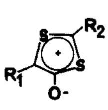
Many five-membered mesionic heterocycles corresponding to the general type (I) have been studied. Extensive reviews have been published on this subject.[1,2]

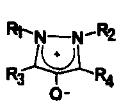

(I)


(II)

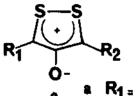
A, B, C and D represent substituted carbon or heteroatoms contributing the indicated number of π electrons to the conjugated system.

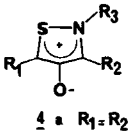
In the 1,3-dithiole series, the structure of 1,3-dithiolylium-4-olate **1** has been studied by different groups, particularly GOTTHARDT *et al.*[3]


1


2

However, few examples of analogous 6π electrons systems corresponding to the general type (II) have been prepared and studied. In the literature the most interesting case is that of pyrazolium-4-olates **2** published by NYE *et al.*[4] In addition the 3,5-diphenyl-1,2-dithiolylium-4-olate **3a** $R_1 = R_2 = —C_6H_5$) has been obtained by OHTA *et al.*[5] and SCHÖNBERG *et al.*[6]


3
a $R_1 = R_2 = C_6H_5$
b $R_1 = R_2 = CH_3\,C_6H_4$
c $R_1 = R_2 = CH_3O\,C_6H_4$
d $R_1 = R_2 = Cl\,C_6H_4$
e $R_1 = R_2 =$ 2-thienyl
f $R_1 = C_6H_5$ $R_2 =$ t-butyl
g $R_1 = R_2 =$ t-butyl
h $R_1 = C_6H_5$ $R_2 = (CH_3)_2NC_6H_4$
i $R_1 = C_6H_5$ $R_2 = SCH_3$
j $R_1 = C_6H_5$ $R_2 = SC_2H_5$
k $R_1 = C_6H_5$ $R_2 = SC_6H_5$


4
a $R_1 = R_2 = C_6H_5$ $R_3 = CH_3$
b $R_1 = R_2 = C_6H_5$ $R_3 = C_2H_5$

A brief structural study has been carried out[6] and recently, POTTS *et al.*[7] also published the results of cycloaddition reactions and an X-ray study with these compounds.

At the same time we prepared a series of 1,2-dithiolylium-4-olates by another route.[8] In this paper we now relate our results with different physical methods and also compare them with some results obtained in the isothiazole series with previously described isothiazolium-4-olates **4**.[9]

IR AND U.V. SPECTROSCOPY

U.V. Visible Spectra

U.V. visible spectra of compounds **3** and **4** were recorded in dioxane, acetonitrile and ethanol (or

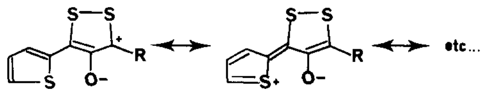
TABLE I

$\pi^* \leftarrow \pi$ transition band in U.V-visible spectra of compounds **3**

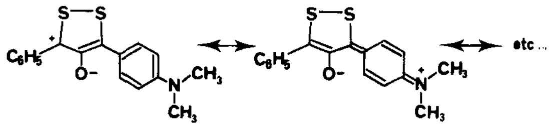
	dioxane λ max (nm)	 ε	acétonitrile λ max (nm)	 ε	éthanol λ max (nm)	 ε
3a[a]	579	5 700	547	31 900	498	28 000
3b[a]	568	46 700	528	23 000	503	26 300
3c[a]	571	17 050	556	7 300	520	24 000
3d[a]	580		557		512	
3e[a]	607	30 400	590	31 300	562	18 100
3f	521	8 000	502	9 080	465	10 700
3g	463	5 950	453	6 290	426	10 020
3h[a]	617		603		574	
3i	543	33 300	525	29 900	478	15 900
3j	545	26 500	527	19 100	482	19 050

[a] the extinction coefficients are approximate or are not given since the poor solubility of the compound in these solvents leads to doubtful concentrations.

methanol). Results are given in Tables I and II. The most characteristic feature is the important negative solvatochromic effect observed for the $\pi^* \leftarrow \pi$ transition band in the region 460–620 nm. For example, in the **3a** case, a displacement of 32 nm occurs in acetonitrile and 81 nm in ethanol. It can be also noted from Table I that the presence of a phenyl substituent results in a bathochromic displacement of this band and that this shift is still greater in the case of compounds **3e** and **3h**. This larger effect results from a wide delocalization of the positive charge which can be rationalized in terms of participation of structures such as a sulfonium form (in the **3e** case) and an ammonium form (in the **3h** case) shown below:



3e R= thiényl



3h

Infrared Spectra

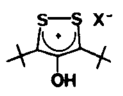
No CO stretching vibration can be observed in the usual carbonyl region of 1600–1800 cm^{-1} from the infrared spectra of compounds **3** and

TABLE II

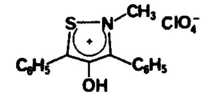
$\pi^* \leftarrow \pi$ transition band in U.V-visible spectra of compounds **4**

	dioxane λ max (nm)	 ε	acétonitrile λ max (nm)	 ε	méthanol λ max (nm)	 ε
4a	491	18 700	466	18 400	414	19 500
4b	490	17 800	463	18 700	412	15 350

4, recorded in KBr. However, a strong band appears near 1500 cm^{-1}, as we described previously.[8,9]



5
X: ClO$_4^-$
or BF$_4^-$



6

The spectra of 3,5 di-*t*-butyl-1,2-dithiolylium-4-olate **3g** were recorded in different solvents and compared with the spectrum of the corresponding perchlorate **5**. Results are collected in Table III.

The band which appears about 1488 cm^{-1} is shown to undergo large solvent shifts. Important hypsochromic displacements of 21 cm^{-1} in CD_3CN and 37 cm^{-1} in C_2Cl_4 can be seen. Moreover, this band does not appear in the spectrum of the corresponding perchlorate **5**. All these observations agree with the assignment of this band to the stretching vibration of a highly polarizable carbonyl. The much lower value of the frequency compared to the value for a 1,2-dithiole-3-one (1630–1700 cm^{-1}) or a mesoionic compound such as sydnone (1720–1770 cm^{-1}) suggests an important polarization $^{\delta+}C—O^{\delta-}$ in the ground

TABLE III

Solvents effects in the i.r. spectra of compound **3g** for the region 1400–1550 cm^{-1}

3g (KBr) cm^{-1}	**3g** (CD_3CN) cm^{-1}	**3g** (C_2Cl_4) cm^{-1}	perchlorate **5** (KBr) cm^{-1}
1488 S	1509 S	1525 S	
1475 m	1483 w	1479 w	1480 S
1463 w	1460 w	1465 w	1460 m
1446 (sh)	1447 S	1448 m	1447 m
1438 S		1442 m	

TABLE IV

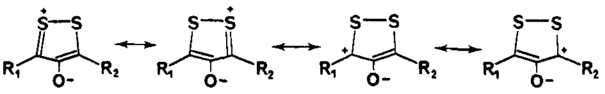
Solvents effects in the i.r spectra of compound **4a** for the region 1400–1600 cm^{-1}

4a (KBr) cm^{-1}	**4a** (CD_3CH) cm^{-1}	**4a** (C_2Cl_4) cm^{-1}	perchlorate **6** (KBr) cm^{-1}
			1576 w
			1564 w
1530 S	1535 S	1543 S	
		1534 (sh)	
1500 m	1505 m	1503 m	1512 m
1493 m	1495 m	1493 m	1495 (sh) w
1476 m	1476 m	1472 m	1474 m
			1450 (sh) m
1439 S	1440 S	1445 S	1439 S

state. Similar results are obtained in the case of isothiazolium-4-olates **4** (about 1530 cm^{-1} in KBr, as can be seen in Table IV). It is of interest to note, on the other hand, that this CO band is given at 1545 cm^{-1} for 1,2-dimethyl-3,5-diphenyl pyrazolium-4-olate **2** by NYE *et al.*[10] which suggests a similarity in the structures of the compounds in the analogous 1,2-dithiol, isothiazole and pyrazole series.

DIPOLE MOMENT MEASUREMENTS

It would be of particular interest to measure the dipole moments of compounds **3a**, or **3c**, **3h** or **3i**. Unfortunately, no accurate data were obtained for these because of their poor solubility in benzene. Dipole moments of the four soluble products were determined from dielectric measurements in benzene solution; results are given in Table V. It can be seen that the experimental values seem to be lower than expected for a zwitterion. The system has been generally expressed till now, by us and others,[5–9] in a general formula which sums the contributions from the structures of type A and B:



A₁ A₂ B₁ B₂

TABLE V

Measured dipole moments (Debye) of some **3** and **4** compounds

Compound	dipole moment
3f	4.43 ± 0.09
3g	3.50 ± 0.01
4a	6.23 ± 0.22
4b	5.26 ± 0.06

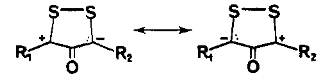
TABLE VI

Calculated dipole moments (Debye[a]) of the canonical structures in compound **3g**.

Structure	$\mu\sigma$	$\mu\pi$	μ (résultant)
$A_1 + A_2$	−1.26	10.7	9.44
$B_1 + B_2$	−1.26	5.86	4.6
$C_1 + C_2$	0.35	0	0.35

[a] Positive values correspond to moments directed from the ring toward the oxygen, negative values to moments directed from the oxygen toward the ring. σ and π moments are estimated on the basis of the geometry of **3a** available with the X-Ray diffraction study (see in this paper).

The theoretical values may be estimated in the case of the symmetrical compound **3g** (Table VI): a value of 9.44 Debye is found for structure A and 4.6 Debye for structure B. Therefore, these structures appear unsatisfactory to account for the lower experimental dipole moment. Therefore contributions from other canonical forms may be considered such as type C, in which the CO is in a carbonyl group: a calculated value of 0,35 D is found in this case.



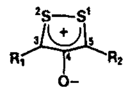
C₁ C₂

If the low experimental value accounts for the nearness of the barycenters of the negative and positive charges, we may conclude that, in the inclusive mesomeric scheme A ↔ B ↔ C, the contribution of resonance structure C is significant.

We may also note that: (a) the dipole moment rises about 1 Debye from **3g** to **3f** because the presence of a phenyl group in this case results in the delocalization of the positive charge separating the positive and negative centers; (b) dipole moments determined for isothiazole derivatives **4a** and **4b** are higher than those observed for **3f** and **3g**. Although substituents are not similar in the two cases, it may be considered that the positive charge is localized on a promotive center like

TABLE VII

Carbon-13 chemical shift[a] data for some compounds 3



3

			Heteroring carbons			Phenyl group				
	R_1	R_2	C_3	C_4	C_5	1′	2′ + 6′	3′ + 5′	4′	Other carbons
3g	*t*-butyl	*t*-butyl	172.4	171.6	172.4	—	—	—	—	40.3 [$C(CH_3)_3$]; 27.7 [CH_3]
3f	*t*-butyl	C_6H_5—	177.2	170.7	153.8	134.2	127.4	128.9	130.7	41.1 [$C(CH_3)_3$]; 27.7 [CH_3]
3i	—SCH_3	C_6H_5—	172.2	167.7	142.5	133.4	127.9	129.1	130.5	16.0 [CH_3]
3j	—SCH_2CH_3	C_6H_5—	170.3	167.9	142.4	133.9	127.3	129.0	130.4	27.5 [CH_2]; 13.7 [CH_3]
3k	—SC_6H_5	C_6H_5—	173.5	167.1	144.5	133.9	127.3	129.1	130.6	134.8 [C_6H_5, 2′ + 6′]; 131.4 [C_6H_5, 4′] 130.9 [C_6H_5, 3′ + 5′]; 128.4 [C_6H_5, 1′]

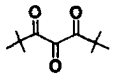
[a] All shifts quoted in ppm relative to TMS in $CDCl_3$ solution.

the nitrogen atom in the case of isothiazolium compounds.

CARBON-13 NUCLEAR MAGNETIC RESONANCE

Spectra of aryl or thienyl disubstituted products **3a–d** could not be recorded because of their poor solubility in usual NMR solvants. Chemical shift data of compounds **3f**, **3g** and **3i–k** are collected in Table VII. In addition to the phenyl group signals (about 130 ppm) and the *t*-butyl or S-alkyl group signals (in the range 13.7–41.1 ppm), three less intensive signals may be assigned to the ring carbons as indicated in Table VII. Chemical shift data of the same heteroring carbons in the spectra of three related 1,2-dithiolylium fluoroborates **5**, **7** and **8** are given in Table VIII.

The first noteworthy point about the spectra of **3** is the C_4 chemical shift (167.1 to 171.6 ppm) which is situated in an intermediate range between the δ^{13} C=O of a ketone, such as 2,2,6,6-tetramethyl heptan-3,4,5-trione **9** (188 ppm), and the δ^{13} C—O found in the case of the fluoroborates **5**, **7** and **8** (153.7–158 ppm).

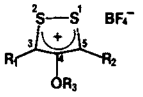


9

Secondly, it may be observed that the C_3 and C_5 resonances are not strongly shifted to low field. For example, in the case of products **3f** (177.2

TABLE VIII

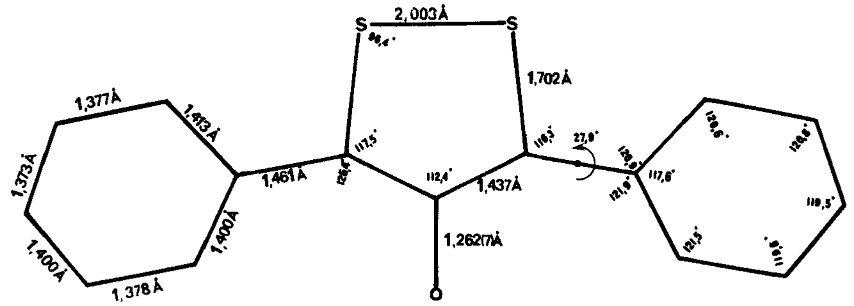
Chemical shifts[a] of the heterocyclic carbons in the ^{13}C. NMR spectra of related 1,2-dithiolylium fluoroborates **5**, **7** and **8**. Chemical shifts effects ($\Delta\,\delta$) between spectra of compounds **3g**, **3f** and **3i** respectively (from Table VII)



5; **7** or **8**

Ref. (solvent)	R_1	R_2	R_3	C_3 δ (ppm)	C_3 $\Delta\,\delta$	C_4 δ (ppm)	C_4 $\Delta\,\delta$	C_5 δ (ppm)	C_5 $\Delta\,\delta$
5	*t*-butyl	*t*-butyl	H	192.3	+19.9	156.9	−14.7	192.3	+19.9
7	*t*-butyl	C_6H_5—	CH_3CH_2—	195.4	+18.2	158.0	—12.8	177.2	+23.4
8	CH_3S—	C_6H_5—	CH_3CH_2—	189.6	+17.4	153.7	−14.0	169.0	+26.5

[a] All shifts quoted in ppm relative to TMS on $CDCl_3$ solution.



ppm) and **3g** (172.4 ppm), the ^{13}C-(t-butyl) chemical shifts are upfield from that of 5-t-butyl-1,2-dithiole-3-thione (188 ppm)[11]. Also, in the case of compound **3i**, the ^{13}C-(SCH_3) and 13C-(C_6H_5) chemical shifts are upfield by an average value of 15 ppm from corresponding resonances in related 6A-thiatophtens given in the literature.[12,13]

Finally, when data from compounds **3** (Table VII) are compared with those from 1,2-dithiolylium salts (Table VIII), the most interesting feature is that the C_3 and C_5 signals are moved downfield by 18 to 26 ppm in the related dithiolylium structure ($\Delta\delta$ effects are given in Table VIII).

Such results may be related by molecular orbital calculations of the parent of compounds **3** carried out by FABIAN[14] with two models: sp and spd. The latter may be more representative than the former of the upfield displacement of the C_3 and C_5 resonance in the spectra of compounds **3** when total and π electron densities are compared in the light of FABIAN's work.

X-RAY DIFFRACTION RESULTS AND DISCUSSION

The crystal structure of compound **3a** has been published recently by CANNON *et al.*[7] At the same time the group of A. HORDWIK has determined the structure for us.[15] The geometry of the molecule which is pictured in Figure 1 is almost identical to the geometry proposed by CANNON *et al.* From these results two main results can be derived:

1) The ring structure is not significantly altered when passing from **3a** to other phenyl-substituted dithiolylium salts.[7,16] π bond characters of 0.45 for the S—S bond and 0.61 for the C—S bond can be evaluated in **3a** with relations formulated by HORDVIK.[17] These values agree with the spd model of FABIAN.

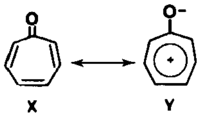
2) If the CO distance is intermediate between those of a carbonyl and a σ CO bond, it seems to approach the carbonyl as can be seen in Table IX. A π bond order of 0.73 has been found by JULG[24] which is also in good agreement with the FABIAN spd model.

On the other hand, it is significant that this CO distance is close to that of tropone. This point of interest leads to comparison between our data and the data from analogous six-π electron systems: tropone **10** and (4H) thiopyran-4-one **11** which are well known.[25–28] It then appears that:

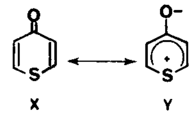
3) The CO stretching vibration is lowered to 1590 cm^{-1} in the case of tropone[29] and to 1600 cm^{-1} in the case of (4H) thiopyran-4-ones.[30,31]

4) A chemical shift $\delta^{13}C(=O)$ of 177.5 ppm is obtained in the case of tropone[32] and of 180 ppm in the case of (4H)thiopyran-4-one.[33]

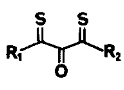
Allowing that the CO groups in compounds **3**, **10** and **11** are similar, the problem of the representation is readily solved in the case of **10** and **11** by using a resonance scheme in which an uncharged form X and a dipolar form Y can be written. Unfortunately, in our case this problem cannot be so easily solved since dipolar forms must necessarily be written: the two uncharged forms D and E or the valence tautomeric structure F, which may introduce a carbonyl in the resonance hybrid, seem to be unreasonable based on our data:



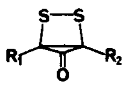
10



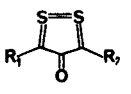
11



D



E



F

TABLE IX

Compared C—O distances (Å) between compound **3a** and some compounds owing an aromatic character

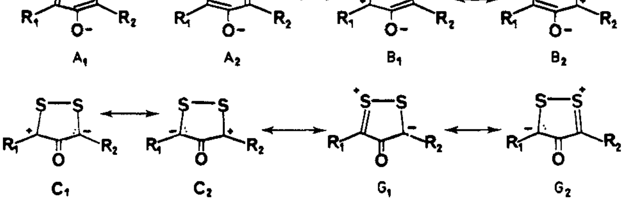
Compound	C— distance	Réf.
3a	1.262	
quinone	1.22	18
2,6-dimethyl-5′-p methoxyphenyl-1,2′dithiole-3′ 4-ylidène-2,5-cyclohexadienone	1.25	19[a]
2-(phenyl-1,2-dithiole-3-ylio)-phenolate	1.301	20
tropone **10**	1.257	21
(4H) thiopyran-4-one **11**	1.27	22
phenol	1.36	23

[a] quinone character of this compound has been established.

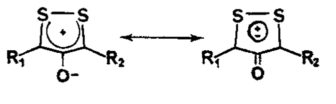
In conclusion, this study shows that the carbonyl of compounds **3** and **4** is not strongly polarized as expected. A π bond character of 0.7, close to tropone, can be estimated but the compounds appear to be highly *polarizable* as shown by the i.r. and u.v. data.

The electronic distribution of compounds **3** is different from the known structures of 1,2-dithiolylium salts,[14,17,34] whereas it seems in closest agreement with the spd model of FABIAN, taking into account that the positive character of C_3 and C_5 are clearly lowered in compounds **3** as shown by ^{13}C. N.M.R. and that the π bond character evaluated from experimental results are in rather good agreement with the theoretical model.

The depiction of the compound remains ambiguous as no representation can satisfactorily relate the various experimental results. We think that the most appropriate solution may be to describe the compound in the ground state as a resonance hybrid in which either A, B, C and G forms can be written and in which the participation of the C and G forms may be significant:



This scheme can be shortened to the following form:



ACKNOWLEDGEMENT

The author thanks Professors J. Vialle and Y. Mollier from the University of Caen, for several helpful discussions and Professor A. Hordvik from the University of Trømsø, for kindly providing X-Ray diffraction results.

EXPERIMENTAL

Physicochemical Measurements

The infrared absorption spectra were recorded on a Perkin Elmer 221 or 225 spectrophotometer. The U.V-visible spectra were recorded on a Beckmann Acta M VI or a Unicam S.P. 700 spectrophotometer.

Dipole moments were determined according to the method of Guggenheim. Dielectric measurements in benzene solution at 20° were carried out with a WTW type DM-01 apparatus and densities were measured using an Anton Park DMA 02C microdensimeter. Molar refractions were estimated from literature increments.[35]

^{13}C N.M.R. spectra were recorded on a Bruker WP 60 Fourier transform N.M.R. spectrometer operating at 15.08 MHz. The number of scans accumulated ranged from 1000 to 11000. The chemical shifts are related to TMS added as internal standard.

Materials

All products **3**, **4**, **5**, **6**, **7** and **8** mentioned in this paper were described previously.[8,9]

The triketone **9** was prepared from previously described[8] 4-acetoxy-2,2,6,6-tetramethyl-3,5-heptanedione **12** according to the method of De Neufville and Von Pechmann.[36]

2,2,6,6-tetraméthyl-3,4,5-heptanetrione 9.

A solution of bromine (3.2 g) in chloroform (10 ml) was added to a stirred solution of compound **12** (5 g) in chloroform (50 ml). After 1 h the crude solution was refluxed for 2 h. Then the solvent was evaporated and the residue distilled under reduced pressure. Compound **9** was obtained as a pale yellow oil (bp=72–73°/15 mm) with a 40% yield. i.r.: C=O (film) = 1695 and 1710 cm^{-1}. ^1H Nmr ($CDCl_3$): δ (ppm) = 1.26 (s). ^{13}C Nmr ($CDCl_3$): δ (ppm) = 25.7 [CH_3]; 42.7 [$C(CH_3)_3$]; 188 [C_4=O] and 208.4 [C_3=O and C_5=O].

REFERENCES

1. M. Ohta and H. Kato, *Non-benzenoid Aromatics*, J. P. Snyder, Ed., tome 1 chapter 4, 117, Academic Press, New York (1969).
2. W. D. Ollis and C. A. Ramsden, *Adv. Heterocycl. Chem.* **19**, 1 (1976).
3. H. Gotthardt, M. C. Weisshuhn, and B. Christl, *Chem. Ber.* **109**, 740 (1976).
4. M. J. Nye and W. P. Tang, *Tetrahedron* **28**, 455 (1972).
5. A. Chinone, K. Inouye, and M. Ohta, *Bull. Chem. Soc. Japan* **45**, 213 (1972).
6. A. Schönberg and E. Frese, *Chem. Ber.* **103**, 3885 (1970).
7. J. R. Cannon, K. T. Potts, C. L. Raston, A. F. Sierakowski, and A. H. White, *Aus. J. Chem.* **31**, 297 (1978).

8. D. Barillier, Ph. Rioult, and J. Vialle, *Bull. Soc. Chim. Fr.* 3031 (1973); *ibid*, 444 (1976); *ibid*, 659 (1977); D. Barillier, *Phosphorus and sulfur*. 251 (1978).
9. D. Barillier, *Bull. Soc. Chim. Fr.* II 26 (1979).
10. M. J. Nye, M. J. O'Hare, and W. P. Tang, *J. Chem. Soc.. Chem. Comm.* 402 (1973).
11. D. Reffet, personal communication.
12. R. D. Lapper and A. J. Poole, *Tetrahedron Letters* 2783 (1974).
13. C. T. Pedersen, *Org. Magn. Res.* **6**, 586 (1974).
14. J. Fabian, *J. prakt. chem.* **315**, 690 (1973).
15. A. Hordvik and K. Jynge, personal communication.
16. A. Hordvik and H. M. Kjøge, *Acta. chem. Scand.* **19**, 935 (1965); A. Hordvik and R. M. Baxter, *ibid*, **23**, 1082 (1969); F. Grundvik and A. Hordvik, *ibid* **25**, 1567 (1971).
17. A. Hordvik, *Acta. chem. Scand.* **20**, 1885 (1966); A. Hordvik and E. Sletten, *ibid* **20**, 1938 (1966).
18. D. Rabinovich and G. M. J. Schmidt, *J. Chem. Soc., Perkin Trans B*, 127 (1967).
19. K. T. H. Wei, I. C. Paul, G. Lecoustumer, R. Pinel, and Y. Mollier, *Tetrahedron Letters*, 2717 (1977).
20. E. C. Llaguno, I. C. Paul, R. Pinel, and Y. Mollier, *Tetrahedron Letters*, 4687 (1972).
21. M. J. Barrow and O. S. Mills, *Chem. Comm.* 66 (1973).
22. D. Gonbeau, personnal communication.; this CO distance has been only evaluated for a molecular orbital calculation on the compound.
23. S. R. Byrn, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.* **94**, 890 (1972).
24. J. Julg, *Theor. Chim. Acta.* **22**, 353 (1971).
25. T. Nozoe, *Non benzenoid Aromatic compounds*, D. Ginsburg, Ed., New York, chapter 7 (1959) and reference cited.
26. C. D. Gutsche, *The chemistry of Carbonyl compounds*, Pentrie Hall, Inc., Englewood Cliffs, N.J., p. 8 (1967) and references cited.
27. D. J. Bertelli and T. G. Andrews Jr., *J. Amer. Chem. Soc.* **91**, 5280 (1969) and references cited.
28. C. C. Price and S. Oae, *Sulfur Bonding*, the Ronald Press Company, New York, p. 20 (1962) and references cited.
29. A. Krebs and B. Schrader, *Ann. Chem.* **709**, 46, (1967).
30. D. S. Tarbell and P. Hoffman, *J. Amer. Chem. Soc.* **76**, 2451 (1954).
31. N. Sugiyama, Y. Sato, H. Kataoka, C. Kashima, and K. Yamada, *Bull. Chem. Soc. Japan*, **42**, 3005 (1969).
32. T. Machiguchi, Y. Inagaki, M. Hoshino, and Y. Kitahara, *Chemistry Letters*, 497 (1974).
33. I. W. Still, N. Plavac, D. M. McKinnon, and M. S. Chauhan, *Can. J. Chem.* **54**, 280 (1976).
34. R. Zahradnik and J. Koutecky, *Coll. Czech. Chem. Commun.* **28**, 1117 (1963).
35. A. I. Vogel, W. T. Cresswell, G. H. Jeffrey, and J. Leceister, *J. Chem. Soc.* 514 (1952).
36. R. de Neufville and H. Von Pechmann, *Ber.* **23**, 3375 (1890).