Thioketyls, 10[1]

The 2,4-Bis(diphenylmethylene)-1,3-cyclobutane-dione Diradical Dianion and its Sulphur Analogues[2]

Thomas Strehlow[*][2][a], **Jürgen Voß**[*][b], **Rüdiger Spohnholz**[b], **and Gunadi Adiwidjaja**[c]

Research Institute for Symbolic Computation[a],
Schloß Hagenberg, A-4232 Hagenberg, Austria

Institut für Organische Chemie der Universität Hamburg[b],
Martin-Luther-King-Platz 6, D-2000 Hamburg 13,

Mineralogisch-Petrographisches Institut der Universität Hamburg[c],
Grindelallee 48, D-2000 Hamburg 13,

Eingegangen am 20. September 1990

Key Words: Cyclobutane-1,3-diones / Cyclobutane-1,3-dithiones / Radical anions / Diradical dianions

2,4-Bis(diphenylmethylene)-1,3-cyclobutanedione (**1**) is transformed into its sulphur analogues **2** and **3** with Lawesson's or Davy's reagent **5a,b**. An X-ray structural analysis is performed on **3**. The electrochemistry of these compounds is surveyed. The products of the electrochemical reduction exhibit ESR spectra, which could not be attributed to the radical anions $\mathbf{1}^{-\bullet}$, $\mathbf{2}^{-\bullet}$, and $\mathbf{3}^{-\bullet}$. Extensive semiempirical AM1/CI calculations suggest the spectra to correspond to the diradical dianions. The experimental data are discussed in terms of the theoretical results.

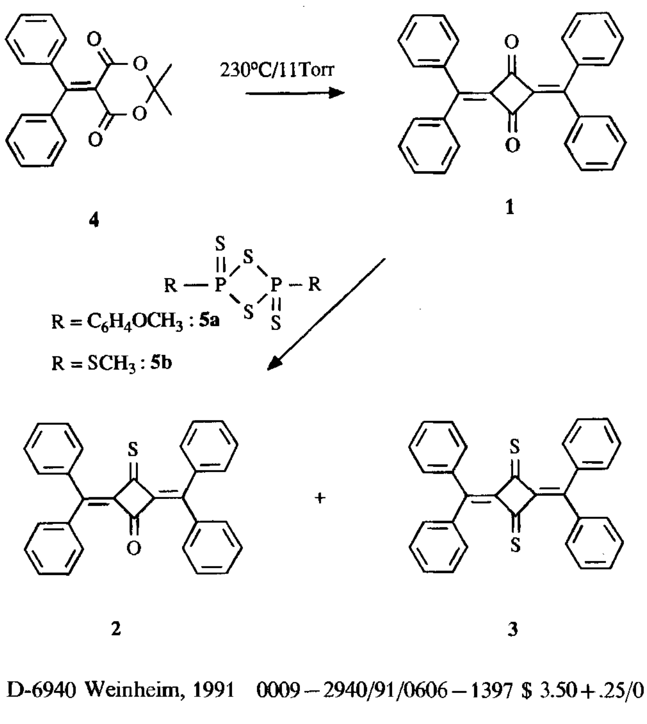
In 1969 Taylor synthesised the diketone **1**[3]. In the course of our investigations of the 2,4-dimethylenebicyclo[1.1.0]-butane system[2], whose synthesis has recently been accomplished by Snyder and Dougherty[4,5], we have prepared substantial amounts of **1**. Since the original synthesis by Taylor has proved to be cumbersome, we have modified Brown's[6] method to make it acceptable to large-scale preparations. The pyrolysis of the Meldrum's acid derivative, which has originally been performed in a flash vacuum pyrolysis apparatus in order to trap the intermediate allenoketenes, proceeds smoothly in a moderately heated flask with evolution of gases which are removed by a water aspirator.

The sulphur analogues are prepared with Davy's[7] or Lawesson's[8] reagents, which nicely substitute the oxygen atoms. The monothio compound **2** is easily isolated from the reaction mixture. The dithione **3** seems to be more delicate. It will either deteriorate or easily polymerise in solution, but once in crystalline form it proves to be stable up to its melting point. On account of the low solubility in any deuterated solvent and the poor relaxation of the thiocar-

Table 1. Selected bond lengths [pm] and angles [°] of **3**

Atom 1	Atom 2	Atom 3	Atom 4	Distance	Angle	Torsion angle
S	C1			162.0		
C1	C2			149.4		
C1	C2'			148.8		
C2	C3			135.6		
C3	C311			147.2		
C3	C321			148.9		
S	C1	C2			136.2	
S	C1	C2'			133.8	
C2	C1	C2'			89.8	
C1	C2	C1'			90.2	
C1	C2	C3			137.3	
C1'	C2	C3			132.2	
C2	C3	C311			125.0	
C2	C3	C321			119.4	
C311	C3	C321			115.7	
C2	C3	C311	C312			36.9
C321	C3	C311	C316			34.6
C2	C3	C321	C326			72.3
C311	C3	C321	C322			71.1

Scheme 1



---

[*] Current address: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2.

Chem. Ber. 124 (1991) 1397–1402 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1991 0009–2940/91/0606–1397 $ 3.50+.25/0

bonyl groups the intensities of the ^{13}C-NMR signals of the thioketone carbons are extremely low. Therefore, the structure has been confirmed by an X-ray diffraction analysis (cf. Table 7). The ORTEP plot is shown in Figure 1. It resembles the structure of the corresponding dione **1**[9], with the phenyl rings rotated out of the cyclobutane plane in the same direction by approx. 35°/72°. The dithione has been found to have a centre of symmetry. Due to the larger sulphur atoms, the two torsion angles of the phenyl rings are slightly different from that of the oxygen compound, which exhibited two significantly different torsion angles of the phenyl rings (34.2°/50.4°). The C=S bond length is 162 pm, and all the other structural features are within reason. A selection of the more characteristic structural parameters is shown in Table 1.

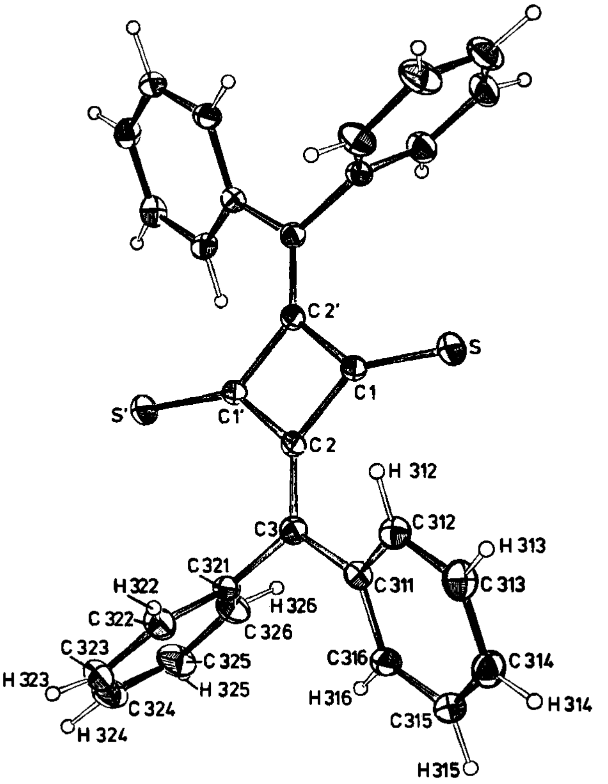


Figure 1. ORTEP plot of the X-ray diffraction analysis of **3**.

Electrochemistry

Enones have been the subject of electroanalytical investigations[10]. Most of these are focused on the reduction to the radical anions, because the reactivity of these reactive intermediates has been felt to be of considerable interest. An ESR investigation[11] shows that in enone radical anions without any hydrogen in the α-position (others have failed to give a spectrum) 40−50% of the spin density reside on the β-carbon. Therefore, they are characterised by reactions on the β-carbon rather than the α-carbon. The same is true for enethione radical anions[12].

The electrochemical reduction of **1** in aprotic media has proved to be highly solvent-dependent. This seems to be a general problem with enones[10,13]. In DMF two waves at −392 and −992 mV are visible. In acetonitrile these are observed at −875 and −1337 mV whereas in THF even three waves could be detected (−775, −1110, and −1585 mV). The first wave corresponds to a highly reversible electron transfer which on addition of water or TMSCl becomes irreversible. The reduction potential of TMSCl itself is approximately −2 V. This would allow to use it as a scavenger of the reactive intermediate products of the reaction[14]. Unfortunately, it is not possible to isolate the reaction products.

Due to the high reversibility of the electron transfer the average lifetime of the radical anion cannot be estimated[15−17] by means of cyclovoltammetry, but it is obvious, that it is long enough to obtain an ESR spectrum of the radical anion. The second reduction wave is irreversible even at high (≫ 1 V/s) scan speeds.

ESR Spectroscopy

The electroanalytical measurements suggest a stable radical anion as the product of the first electron-transfer wave. The distribution of the spin density is of considerable interest since bicyclobutane structures have been formulated for the tetramethylcyclobutanedithione radical anions[18]. Therefore, an ESR spectrum has been taken during the in-situ electroreduction of **1**, **2**, **3** in DMF or acetonitrile. The spec-

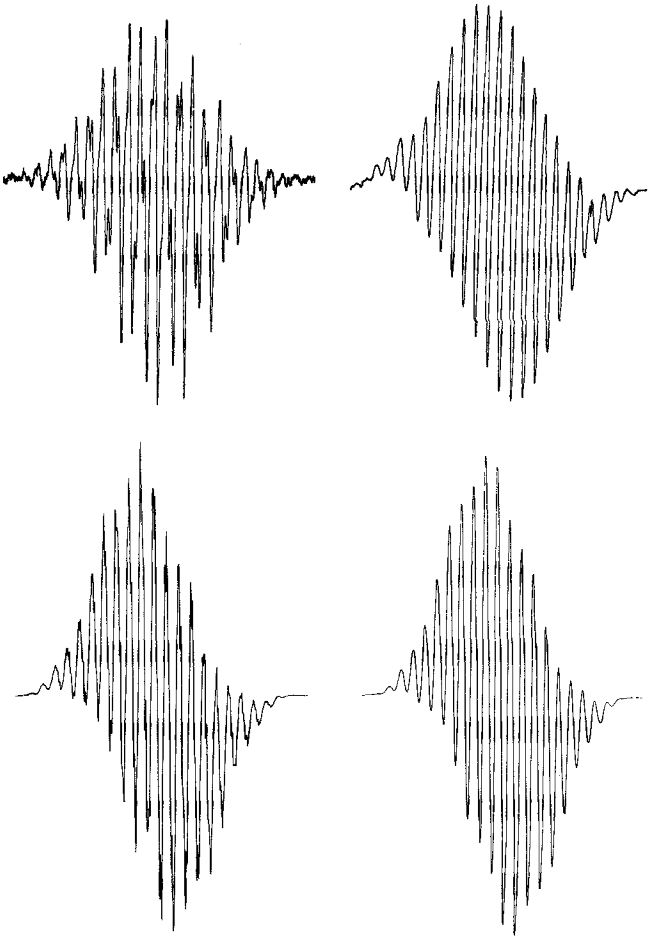


Figure 2. Experimental (top) and simulated (bottom) ESR spectra of the reduction products of **1** (left) and **2** (right)

tra of the thione radical anions seem to be alike, whereas that of **1** exhibits a significantly higher resolution (cf. Figure 2). It is known that spectra with many coupling protons tend to hide the information in the poorly resolved and less intense outer parts of the spectrum. To ensure that the spectra taken are from different species, we have repeatedly measured the g factors of the three compounds. The obtained values have proved to be reproducible. The values in DMF are $g_{1^{-\cdot}} = 2.0043$, $g_{2^{-\cdot}} = 2.0041$, and $g_{3^{-\cdot}} = 2.0032$, respectively.

The g-factor quoted for aliphatic enone radical anions is 2.0038[11] and that for enethione radical anions is 2.0050 to 2.0068[12]. On these the unpaired electron cannot be delocalised over a large π orbital extending far away from the heteroatoms, and thus they exhibit higher g factors on account of spin-orbit coupling (heavy-atom effect of the oxygen and sulphur atoms). By contrast, the value for $\mathbf{1}^{-\cdot}$ is very low (the value for the free electron in HMPA/THF is 2.0022!) and reflects the wide distribution of the electron. This is even more obvious for the radical anions of **2** and **3**.

The proton h.f.s. coupling constants found by simulation of the spectrum are $a_1^H = 0.175$ mT (4 H_p), $a_2^H = 0.065$ mT (4 H_o), and $a_3^H = 0.045$ mT (4 H_o), $a_4^H = 0.010$ mT (8 H_m) for the radical anion of the dione **1**. The spectra of the sulphur substituted compounds are remarkably similar, the influence of the heteroatoms is hardly visible in the spectra. The following proton h.f.s. coupling constants have been obtained: $a_1^H = 0.175$ mT (4 H_p), $a_2^H = 0.0585$ mT (4 H_o) and $a_3^H = 0.0525$ mT (4 H_o), $a_4^H = 0.012$ mT (8 H_m). The difference between the two *ortho* couplings is not as pronounced as in the dione radical anion. The *meta* coupling disappears in the line width and does not contribute to the number of lines.

AM1 Calculations

Due to the fact, that the data obtained by EPR spectroscopy are difficult and not unambiguously to establish by simulation of the spectra, we decided to perform AM1 calculations on the system. This yields a more detailed view of the situation. To handle the big systems the AMPAC[19] program has been opened up to take 52 atoms and recompiled. The hardware used are a microVax II and some Vax working stations. First a closed-shell calculation of the uncharged species **1**, **2**, and **3** has been undertaken and the fully optimised geometry compared with the geometries obtained from X-ray crystallographic analyses[9]. Although a perfect matching cannot be expected due to crystal lattice effects in the crystalline compounds, the geometries resembled each other to a large extent and have served as a reasonable starting point for the charged species. A compilation of the relevant data is given in Table 2. The optimized geometries of **1** and **3** are shown in Figures 3 and 4[20].

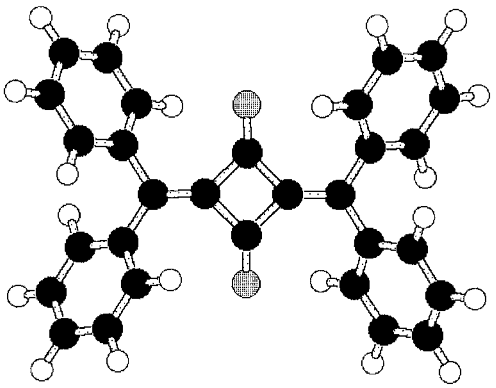


Figure 3. Calculated geometry of the uncharged dione **1**

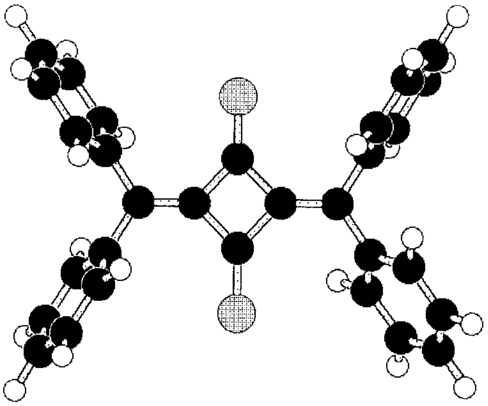


Figure 4. Calculated geometry of the uncharged dithione **3**

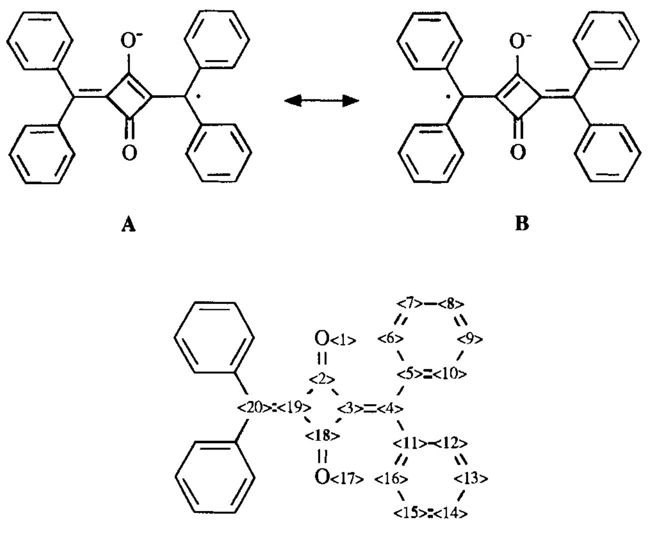
The major differences in the structures lie in the too short C=S bond in the calculated geometries, which is a well-known weakness of the method employed, and the torsion angle of the phenyl rings relative to the cyclobutane unit. All the phenyl rings are twisted in the same direction as has been found in the original publication of the X-ray crystallographic analysis of the dione **1**. In the X-ray structure two different torsion angles have been detected for the com-

Table 2. Experimental and calculated bond lengths [pm], torsion angles [°], and calculated enthalpies of formation ΔH [kJ·mol^{-1}] of **1**–**3**

compnd	C=O^{exp}	C=O	C=S^{exp}	C=S	C=C^{exp}	C=C	Torsion^{exp}	Torsion	ΔH
1	120.6	124.6			136.1	134.3	34.2	41.48	-910
							50.4	43.73	
2		126.1		155.9		134.3		53.99	-378
3			162.0	155.7	135.6	134.0	36.9	75.54	128
							34.6		

pound **1**, whereas for the dithione **3** we have found, that these two angles are slightly different from those of **1**. Thus, the dithione as well as the diketone have a centre of symmetry. The calculations, however, yield molecules with even higher symmetry for both species. All four phenyl rings appear to be twisted out of the bicyclobutane plane by the same amount. The loss of symmetry in the crystallised compound is probably due to lattice effects, whereas in vacuo there is no advantage in terms of energy by using two different torsion angles. The semiempirical calculations have first been performed with full optimization of all parameters, but it has been found, that the introduction of symmetry leads only to marginal errors in these calculations (cf. Table 3 and 4) and can be effectively used to shorten the computation time in subsequent calculations. After having generated the three optimized geometries of the uncharged species as starting geometries for the radical anions, we have performed CI calculations (using five states). By far the highest spin densities are detected on atoms 4 and 20, whereas the highest charge densities are found on the heteroatoms. The values are given in Table 4. The situation is best represented by a set of mesomeric forms whose weight is mostly on the formulae **A** and **B**, which is in contrast to the situation of the radical anion of the tetramethyl derivative.

Scheme 2. Mesomeric forms of $\mathbf{1}^{-\bullet}$ with the numbering system used in the calculations



Numbering of the atoms

The geometries and spin density distributions on the p_z orbitals of the phenyl carbons obtained are listed in Tables 3 and 4.

Table 4. Calculated bond lengths [pm], torsion angles [°], enthalpies of formation [kJ·mol^{-1}], spin densities ϱ [10^{-4}], and heteroatom charge σ of $\mathbf{1}^{-\bullet}$

compnd	C=O	C=C	Torsion	ΔH	ϱ_4	ϱ_{20}	σ
$\mathbf{1}^{-\bullet}$	126.1	135.9	38.6	-1097	1721	1917	-0.3754
		136.4	36.5				
$\mathbf{1}^{-\bullet}$sym	124.7	136.2	38.5	-1093	1843	1816	-0.3664

A correlation of the calculated spin densities with the coupling constants of the experimental spectrum according to the McConnell equation,

$$a^{H}_{C-CH} = -2.4 \cdot \varrho^{\pi}_{\mu}$$

looks disappointing at first view. The theoretical and experimental values do not agree. This awkward situation has urged us to reconsider the situation. Having in mind that each enone moiety should be amenable to a one-electron reduction and both are not distinguishable by constitution, it has seemed possible that the recorded ESR spectra we had taken stem from a diradical dianion. Thus AM1 calculations have been performed on the triplet diradical dianion. The resulting coupling constants fit the data from our simulation of the experimental spectrum much better. The data are given in Table 5. The geometry of the dianion (cf. Table 6) is remarkably similar to that of the uncharged species, the main difference concerning bond lengths. The triplet diradical dianion has been assumed to be lower in energy than the corresponding diamagnetic singlet dianion according to theoretical and spectroscopic work on related compounds[4,21,22]. Further investigations are under way to survey the energy gaps between the triplet, singlet, and covalent species. According to the spin density and charge distribution taken from the semiempirical calculations the resonance structures **C**, **D**, **F**, and **G** contribute most, whereas structure **E** seems to have little significance. The AM1 calculations strongly suggest that the species formed in the electroreduction of **1**–**3** are diradical dianions rather than simple radical anions. The spin density is concentrated on atoms 3, 19 and 4, 20 rather than the carbonyl carbon atoms, and the negative charge resides mainly on 3, 19 and the heteroatoms. Thus, the electrochemical reduction of **1** does not lead to a species containing the elusive dimethylene-bicyclobutane structural unit.

Table 3. Spin densities ϱ [10^{-4}] of $\mathbf{1}^{-\bullet}$

reduced compnd	phenyl ring 1 ortho	phenyl ring 1 meta	phenyl ring 1 para	phenyl ring 2 ortho	phenyl ring 2 meta	phenyl ring 2 para	phenyl ring 3 ortho	phenyl ring 3 meta	phenyl ring 3 para	phenyl ring 4 ortho	phenyl ring 4 meta	phenyl ring 4 para
$\mathbf{1}^{-\bullet}$	75	8	115	75	3.7	115	94	9	142	95	4	135
	78	6		76	6.9		99	5		85	8	
$\mathbf{1}^{-\bullet}$sym	82	8	129	89	5	130	77	7	122	79	4	116
	89	4		82	7		86	4		73	7	
observed	270	29	729									
exp. values	188											

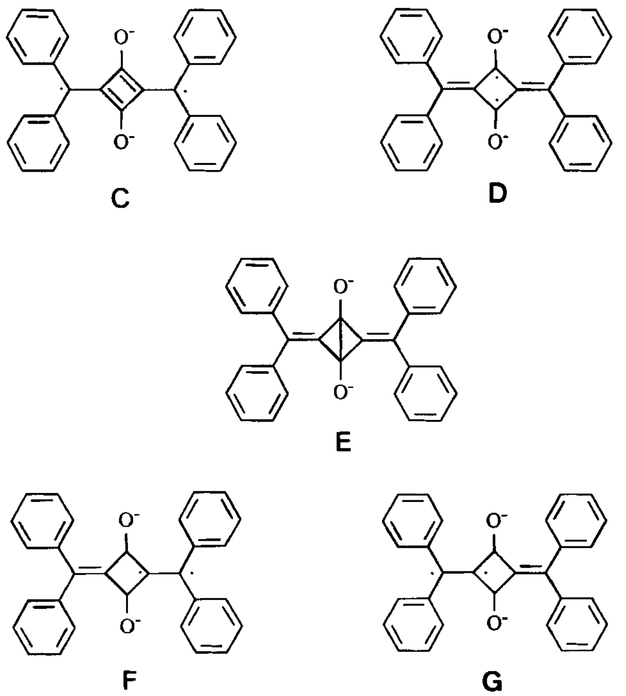
Table 5. Spin densities ϱ [10^{-4}] of the diradical dianions $\ddot{1}^{-2}$, $\ddot{2}^{-2}$, and $\ddot{3}^{-2}$

	phenyl ring 1			phenyl ring 2			phenyl ring 3			phenyl ring 4		
compnd	ortho	meta	para	ortho	meta	para	ortho	meta	para	ortho	meta	para
1^{2-}sym	189	90	487	288	45	513	189	88	484	268	40	474
	270	38		209	84		266	42		184	87	
2^{2-}	176	84	462	284	33	476	191	90	495	270	33	461
	271	35		177	91		285	37		174	87	
3^{2-}sym	187	67	414	218	34	393	173	68	386	239	55	423
	220	41		151	63		211	32		179	49	
observed values	188	29	729									
(red. of **1**)	270											

Table 6. Bond lengths [pm], torsion angles [°], enthalpy of formation [kJ·mol^{-1}], spin densities ϱ [10^{-4}], and heteroatom charge σ of the dianions

compnd	C=O	C=S	C=C	Torsion	ΔH	ϱ_4	ϱ_{20}	ϱ_3	ϱ_{19}	σ
1^{2-}sym	125.0		138.3	31.8	-936	1693	1750	2161	2150	-0.4035
2^{2-}	123.3	160.0	138.7	35.9	-439	1515	1489	2143	2144	-0.2894
										-0.3749
3^{2-}sym		157.2	139.2	38.9	-173	1974	1927	1720	1710	-0.2932
1^{2-}	125.5		138.6	37.6	-966					-0.4100
1^{2-}sing	125.9		138.8	33.4	-965					-0.4525

Scheme 3. Resonance formulae of the diradical dianion of **1**



This work was supported by the *Fonds der Chemischen Industrie*. T.S. acknowledges a scholarship of the ***Freie und Hansestadt Hamburg*** and the ***RISC Institute*** is thanked for a generous supply of CPU time.

Experimental

NMR: Bruker WM 400 or WH 270, $CDCl_3$ as solvent, TMS as internal standard unless otherwise stated. – IR: Perkin Elmer 399, KBr pellets. – VIS: Perkin Elmer U 200. – MS: Finnigan CH 7 or 311 A or VG-analytical 70–250 S. – Electrochemical measurements: Bruker 310 polarograph and Metrohm polarography stand. All potentials were measured vs. the SCE. – EPR: Bruker ER 420s with a special cell described in ref.[1].

2,4-Bis(diphenylmethylene)-1,3-cyclobutanedione (**1**): 2,2-Dimethyl-5-(diphenylmethylene)-1,3-dioxane-4,6-dione[23] (11.5 g, 37.3 mmol) was placed in a 250-ml flask equipped with a condenser. The top of the condenser was connected to a water aspirator. Under permanent suction of the pump the temperature was slowly increased to 200–230°C by means of a silicon oil bath. The temperature was maintained for about 1 h until the gas evolution ceased. The dark brown residue was crystallised from toluene to yield 6.46 g (42%) of dark red needles: m.p. 297–298°C (ref.[6] 315°C; ref.[3] 295 °C). – ^{13}C NMR (100.62 MHz): δ = 127.9, 131.59, 132.28, 136.14, 152.43, 155.9, 186.56 (C=O). – VIS (cyclohexane): λ_{max} = 452, 423 nm.

2,4-Bis(diphenylmethylene)-3-thioxo-1-cyclobutanone (**2**): 0.50 g (1.2 mmol) of **1**, 50 ml of toluene, and 2.5 g of Davy's reagent[7] or Lawesson's reagent[8] were gently heated at reflux for 1 h with stirring. The progress of the reaction could be monitored by TLC (silica gel/dichloromethane). The mixture was poured onto an alumina (act. I, neutral) column, eluted with chloroform and the resulting product crystallised from toluene. Lustrous, dark violet crystals, 0.3 g (58%), m.p. 207–208°C. – IR: ṽ = 1745, 1540, 1340, 1040, 780, 700 cm^{-1}. – ^{13}C NMR (CD_2Cl_2, 100.62 MHz): δ = 128.2, 128.34, 131.31, 132.38, 133.10, 133.24, 136.26, 137.97, 151.69, 158.4, 185.52 (C=O), 224.56 (C=S). – MS (70 eV): *m/z* = 428 [M^+]. – VIS (cyclohexane): λ_{max} (lgε) = 456 nm (4.129), 354 (2.525).

$C_{30}H_{20}OS$ (428.55) Calcd. C 84.08 H 4.70 S 7.48
Found C 83.94 H 4.72 S 7.50

2,4-Bis(diphenylmethylene)-1,3-cyclobutane-dithione (**3**): 0.60 g (1.46 mmol) of **1**, 50 ml of toluene, and 3.0 g of Davy's reagent[7] or Lawesson's reagent[8] were refluxed gently for 3–4 h. The reaction mixture was poured onto an alumina (act. I, neutral) column and eluted with dichloromethane. Crystallisation of the resulting crude product from toluene gave black crystals with a metallic lustre;

0.24 g (37%), m.p. 222–223°C. – IR: $\tilde{\nu}$ = 1510, 1480, 1440, 1325, 1300, 1225, 1175, 780, 750, 690 cm^{-1}. – ^{13}C NMR (67.925 MHz): δ = 127.69, 131.06, 132.72, 137.07, 147.83, 150.34, 242.7 (C=S). – VIS (cyclohexane): λ_{max} (lgε) = 478 nm (4.407), 361 sh. – MS (70 eV): m/z = 444.0976257 ($C_{30}H_{20}S_2$) (ber. 444.1006).

X-ray Structure Analysis of **3**[24]: Black-violet prisms, $C_{30}H_{20}S_2$, M = 444.62, space group $C2/c$, a = 2057.3(2), b = 600.0(1), c = 1934.8(2) pm, β = 106.28(1)°, V = 2293 · 10^6 pm^3, Z = 4, d_{calc} = 1.29 gcm^{-3}, linear absorption coefficient, μ = 21.62 cm^{-1}, Cu-K_α radiation, Enraf Nonius CAD 4-SP diffractometer, graphite monochromator; $\Theta/2\ \Theta$-scans, 2 Θ-range: 2–70°; number of significant symmetrically independent reflections: 1882, $I \geq 3\sigma(I)$; direct methods (MULTAN[25]) and differential Fourier synthesis, refinement by least-squares methods; R = 0.036, R_w = 0.034; $w = \sigma I^{-2}$; max. in diff. map: 0.34 e $Å^{-3}$. Atomic coordinates are given in Table 7.

Table 7. Atomic coordinates of **3** with standard deviations

Atom	X	Y	Z	B
S	0.14838(2)	0.0827(1)	0.54496(3)	4.39(1)
C1	0.21011(8)	0.1777(3)	0.51672(9)	2.95(4)
C2	0.28553(8)	0.1566(3)	0.53900(9)	2.91(4)
C3	0.33361(8)	0.0516(3)	0.59136(9)	2.93(4)
C311	0.32012(8)	-0.1202(3)	0.63986(9)	2.98(4)
C312	0.26906(9)	-0.2791(3)	0.6169(1)	3.51(4)
C313	0.2587(1)	-0.4392(4)	0.6641(1)	4.11(4)
C314	0.2980(1)	-0.4418(4)	0.7346(1)	4.25(5)
C315	0.3487(1)	-0.2865(4)	0.7580(1)	4.06(5)
C316	0.36060(9)	-0.1290(4)	0.7112(1)	3.56(4)
C321	0.40614(8)	0.1121(3)	0.60311(9)	3.19(4)
C322	0.4498(1)	-0.0360(4)	0.5849(1)	4.53(5)
C323	0.5172(1)	0.0212(5)	0.5958(1)	5.81(6)
C324	0.5413(1)	0.2209(5)	0.6275(1)	6.18(6)
C325	0.4983(1)	0.3659(5)	0.6475(2)	6.00(7)
C326	0.4306(1)	0.3139(4)	0.6344(1)	4.62(5)

CAS Registry Numbers

1: 21086-24-8 / $\mathbf{1}^{-\bullet}$: 132776-41-1 / / $\ddot{\mathbf{1}}^{-2}$: 132880-49-0 / **2**: 132776-39-7 / $\mathbf{2}^{-\bullet}$: 132776-42-2 / $\ddot{\mathbf{2}}^{-2}$: 132880-50-3 / **3**: 132776-40-0 / $\mathbf{3}^{-\bullet}$: 132776-43-3 / $\ddot{\mathbf{3}}^{-2}$: 132881-65-3 / **4**: 13311-00-7

[1] 9. Mitteilung: D. Buddensiek, B. Köpke, J. Voß, *Chem. Ber.* **120** (1987) 575.

[2] T. Strelow, *Dissertation*, Univ. Hamburg, 1987.

[3] G. A. Taylor, *J. Chem. Soc. C* **1969**, 1755.

[4] G. J. Snyder, D. A. Dougherty, *J. Am. Chem. Soc.* **111** (1989) 3927.

[5] G. J. Snyder, D. A. Dougherty, *J. Am. Chem. Soc.* **111** (1989) 3942.

[6] R. F. C. Brown, F. W. Eastwood, K. J. Harrington, *Austr. J. Chem.* **27** (1974) 2373.

[7] H. Davy, P. Metzner, *J. Chem. Res. (S)* **1985**, 272 (*M*) 2701.

[8] B. S. Pedersen, S. Scheibye, N. H. Nilsson, S.-D. Lawesson, *Bull. Soc. Chim. Belg.* **87** (1978) 223, 293.

[9] B. M. Gatehouse, *Cryst. Struct. Commun.* **11** (1982) 369.

[10] M. M. Baizer, R. D. Little, *The Chemistry of Enones* in *The Chemistry of Functional Groups* (S. Patai, Z. Rappoport, Eds.) Wiley, Chichester 1989.

[11] W. Schmüser, J. Voß, *J. Chem. Res. (S)* **1980**, 262 (*M*) 3361.

[12] K. W. Bowers, R. W. Giese, G. Jrimshaw, H. O. House, N. H. Kolodny, K. Kronberger, D. K. Roe, *J. Am. Chem. Soc.* **92** (1970) 2783.

[13] M. M. Baizer, L. G. Feoktistov in *Organic Electrochemistry*, 2nd Ed., chapter 10 and 20, pages 359–373 and 658–673, Dekker, New York 1983.

[14] Th. Troll, G. W. Ollmann, *Electrochim. Acta* **29** (1984) 467.

[15] J. Müller, D. Kersten, K. H. Heckner, *Z. Phys. Chem. (Leipzig)* **254** (1973) 387.

[16] R. S. Nicolson, *Anal. Chem.* **38** (1966) 1406.

[17] R. S. Nicolson, I. Shain, *Anal. Chem.* **36** (1964) 706.

[18] L. Kistenbrügger, C.-P. Klages, J. Voß, *J. Chem. Res. (S)* **1979**, 320 *(M)* 3656.

[19] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **107** (1985) 3209. QCPE Program No. 506, Bloomington, Indiana, USA.

[20] J. M. Cense, *Moldraw Program. Tetrahedron Computer Methodology* **2** (1989) 65.

[21] P. H. M. Budzelaar, E. Kraka, D. Cremer, P. v. R. Schleyer, *J. Am. Chem. Soc.* **108** (1986) 561.

[22] D. Feller, E. R. Davidson, W. T. Borden, *J. Am. Chem. Soc.* **104** (1982) 1216.

[23] G. A. Bihlmeyer, F. J. Kunz, O. E. Polansky, *Monatsh. Chem.* **97** (1966) 1293.

[24] Further details of the crystal structure investigation are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54841, the names of the authors, and the journal citation.

[25] G. Germain, P. Main, M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27** (1971) 368.

[321/90]