A THEORETICAL STUDY OF THE DISULFIDE/DITHIONE VALENCE ISOMERISM*

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

According to MNDO calculations on 1,2-dithiete (*IIIa*), 1,2-dithiin (*IVa*) and 3,4-dimethylene--1,2-dithiane (*Va*) the closed-ring compounds are thermodynamically more stable than the open--chain compounds whereas the reverse holds for 4-methylene-1,2-dithiole (*VIa*). Substitution of the exocyclic CH_2 group of *VIa* by O, S, NH, and OH^+ stabilizes its cyclic mesoionic structure. The low triplet state energy of *VIa* and of some derivatives relative to the lowest singlet state energy signalizes the biradicaloid nature of these electronic structures. Replacement of hydrogen of the methine groups adjacent to sulfur of *III*, *IV*, and *VII* by CH_3, CF_3, C_6H_5, CHO or CN results more or less in stabilization of the cyclic tautomer whereas donor substituents such as NH_2, OCH_3 or SCH_3 act less uniformly but mostly in a destabilizing way. Contrary to former assumptions, there is no indication for a species intermediate between the disulfide and dithione structure that defines the molecular ground state. A relatively low ground state barrier separates the two isomeric structures although thermal isomerization of *IIIa* belongs to Woodward--Hoffmann forbidden concerted reactions (calculated activation energy for the ring opening of *IIIa* about 36 kcal/mol).** The thermal and photochemical isomerization is discussed in terms of the change of the energy along the reaction path of the closed shell ground state (S_0) and lowest energy excited states (S_1, T_1). The energies are obtained by MNDO, MNDO/2 × 2 CI, MNDO/HE, and MNDO/HE/3 × 3 CI calculations.

It was not until the late fifties and early sixties that organic sulfur chemists became aware of the stimulating impact of quantum chemical models. Rudolf Zahradník was the pioneer in this field realizing the strength of the quantum chemistry by treating whole families of compounds semi-empirically[1]. His enthusiastic engagement and power of personality affected even conservative experimentalists and resulted in first joint projects with organosulfur chemists[2]. Since than his conceptual approach to problems of chemistry has found extensive application making use of increasingly refined semiempirical methods up to *ab initio* treatments.
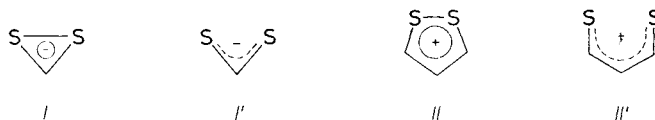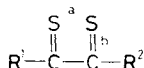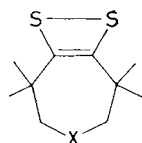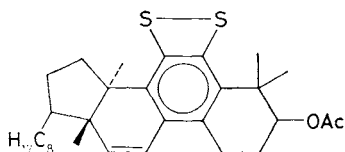
In formulae *III, III′*   *a*, R = R² = H
b, R′ = R² = Me   *c*, R′ = R² = t-Bu
d, R′ = t-Bu ; R² = H   *e*, R¹ = t-Bu ;
R² = NMe ;   *f*, R¹ = R² = CF₃
g, R′ = R² = C₆H₅   *h*, R¹ = R² = p-Me₂NC₆H₄
i, R′ = R² = NH₂   *j*, R¹ = R² = OMe
k, R′ = R′ = SMe   *l*, R¹ = R² = CH₂—S—CH₂
m, R = SMe ; R² = NMe₂   *n*, R² = NMe₂ ;
R = p-t-BuC₆H₄   *o*, R¹ = R² = CHO
q, R = R′ = CN   *r*, R¹ = R² = CH=CH—CH=CH

III s, X = CH₂, S, SO₂

III t
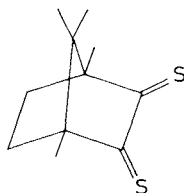
III′ u
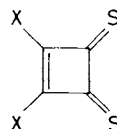
III′ v, X = SR, NR₂
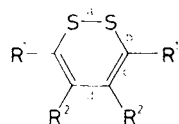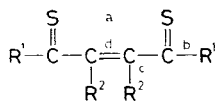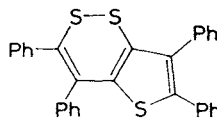
In formulae *IV, IV′*:   *a*, R′ = R² = H   *b*, R¹ = Me ; R² = H
c, R′ = Bu ; R² = H   *d*, R′ = CF₃ ; R² = H   *e*, R¹ = C₆H₅ ; R² = H
f, R′ = NH₂ ; R² = H   *g*, R′ = OMe ; R² = H   *h*, R¹ = SMe ;
R² = H   *i*, R¹ = CHO ; R² = H   *j*, R¹ = CN ; R² = H
k, R′ = CCR ; R² = H   *l*, R′ = R² = CH=CH—CH=CH
m, R′ = R² = SCF₃   *n*, R¹ = N=CR₂ ; R² = CN   *o*, R′ = piperidyl ;
R² = COOMe   *q*, R¹ = 2-thienyl ; R² = H

IV r
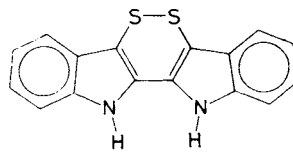
IV s
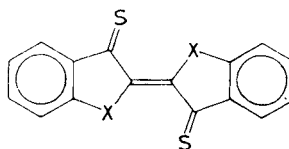
IV′ t, X = NH, S

This paper deals with some simple conjugated heterocyclic disulfides of different ring size (*I* to *VII*). This class of compounds has received less attention so far compared with other series of sulfur heterocycles both from experimental and theoretical point of view.
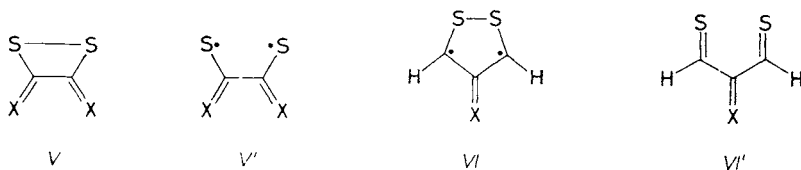
In formulae *V* - *V'* : *a*, X = CH$_2$ *b*, X = O   *c*, X = S   *d*, X = NH   *e*, X = OH$^+$
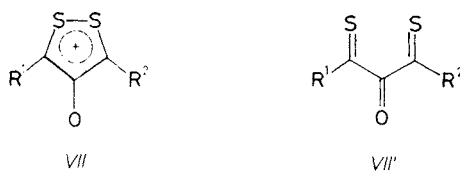
In formulae *VII*, *VII'* :   *a*, R^1 = R^2 = H   *b*, R^1 = R^2 = Me
c, R^1 = R^1 = t - Bu   *d*, R^1 = t-Bu ; R^2 = PhCONH
e, R^1 = R^2 = Ph   *f*, R^1 = R^2 = NH$_2$ *g*, R^1 = R^2 = OMe
h, R^1 = R^2 = SMe   *i*, R^1 = SMe ; R^2 = NH$_2$ *j*, R^1 = R^2 = CHO
k, R^1 = R^2 = CN   *l*, R^1 = R^2 = 2 -thienyl

Ring-opening by cleavage of the weak S—S bond may result in isomeric open-chain dithiones (*I'* to *VII'*). Attempts to assign these compounds to one or the other valence isomer has often led to controversial discussions. The situation appears even more intricate when a single species of the structure *A/A'* is invoked instead of the two isomers *A* and *A'* as detailed above (*A* : *I* to *VII*).
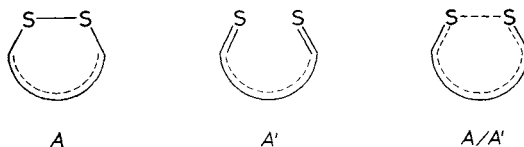
The most simple singly charged dithio compounds are either acyclic such as *I'* (dithioformate)[3] or cyclic such as *II* (dithiolylium)[4] but the structure is less evident for various non-charged conjugated dithio compounds. The 1,2-dithiete structure

(*III*) has been confirmed for *IIIf* (ref.[5]), *IIIs* (X = S, ref.[6]) and *IIIt* (ref.[7]) by diffraction studies and, more recently, also for the parent compound *IIIa* by the rotational spectrum[8]. Compound *IIIa* has even been discerned at 620° in the gas phase[9]. For additional compounds such as *IIIb* (ref.[9]), *IIIc* (ref.[10]), *IIIr* (ref.[11]), and *IIIs* (X = = CH_2, SO_2, ref.[12]) serious arguments have been put forward in favour of the ring structure by means of UV/VIS, NMR or PE spectral data. Attempts failed[11,13] to obtain dithiones such as *o*-dithiobenzoquinone *III'r* and its diamino-substituted derivatives[14], but rubeanic acid (*III'i*) is definitely of non-cyclic structure. According to the X-ray diffraction study *III'i* exists in the *s-trans* (*anti*) conformation in the crystal[15]. Open-chain structures are also encountered with many other dithio-oxamides[16·] and with bis(*p*-dimethylamino)dithiobenzil[17] (*III'h*), which can be considered as phenylogue of dithiooxamide. Spectroscopic data furnished evidence for the open-chain structure of *III'e* (ref.[10]), *III'j* (ref.[18]), *III'k* (refs[9,19]), *III'l* (ref.[9]), *III'u* (ref.[20]), and *III'v* (ref.[21]). As demonstrated by de Mayo[17,20] and coworkers dithiones are converted into isomeric dithietes (and vice versa) by irradiation in alcoholic glasses at 77 K (*III'a, III'd*) or in CH_2Cl_2 at 272·6 K (*III'h*). No dark equilibration has been observed at 77 K. The presence of two isomers in solution has been postulated[22] in view of the NMR chemical shift of *III'm* and the effect of temperature and solvents on the isomeric equilibrium of *III'h* has been thoroughly studied by UV/VIS spectroscopy[17].

Whilst 1,2-dithietes (*III*) possess a sextet of π-electrons 1,2-dithiins (*IV*) contain an 8π-electronic system. The parent compound *IVa* and some derivatives such as *IVe* and *IVq* have been synthesized by Schroth and coworkers[23]. Some naturally occurring acetylenes derived from *IVk* also belong to this series[24]. Early papers have attributed them the dithione structure[25] but more recent ones[26] prefer the dithiin structure[25]. The real structure of these natural products, however, remained unknown[27]. The question has even been posed[25] as to whether a single species exists in place of the two isomeric compounds. This species is assumed to be of intermediate structure such as visualized by no bond resonance structures or by the general formula *A/A'* depicted above. Recently this question has been revived[28] in connection with the preparation of *IVn*. Spectral data led to the conclusion that *IVa, IVe, IVq* and further aryl-substituted-*IV* are cyclic compounds[23,29]. Most recently recorded ^{13}C NMR spectra have convincingly confirmed that these compounds are not dithiones in solution[30]. Dibenzo[*c,e*]dithiin (*IVl*) is the only compound the structure of which has been established by X-ray crystallographic analysis[31]. This molecule is puckered in the crystalline state. The planes of the benzenoid rings are inclined to each other by 34° giving rise to the CSS/SSC dihedral angle of 68·7°. Some more recently synthesized compounds such as *IVc* (ref.[32]), *IVm* (ref.[33]), *IVn* (ref.[28]), R = Ph, *IVo* (ref.[34]), and *IVr* (ref.[35]) have been tentatively assigned to the heterocyclic series. The dithiin *IVs* is assumed to be formed instead of the dithiono indigo (*IVt*, X = NH) expected[36] whereas related dithiono thioindigo the dithione

structure has been attributed[37] $(IV't,$ X = S). In contrast to a former ^{13}C NMR study of dithiins such as IVb and IVe doubling of the signals at room temperature has been recently reported[32] for $IVc.$ This finding has been discussed in terms of two non-planar conformations of the heterocyclic molecule. Attempts failed[38] to synthesize $IVg.$ O,O-Diethyl dithiofumarate $(IV'g)$ did not undergo photoisomerization.

Various compounds of the 1,2-dithiole series VII (1,2-dithiolylium-4-olates) such as $VIIc - VIIe$ and several further aryl- and heteroaryl-substituted compounds have been synthesized[39-41]. The ring structure of $VIIe$ and $VIII$ is supported by X-ray diffraction studies[42]. On the other hand, an open-chain tautomer is encountered[43] in the morpholino-substituted VII' $(VII'f,$ morpholino instead of NH_2). Structures of compounds bearing alkylamino and alkylthio groups have recently been examined by UV/VIS spectroscopy[40]. Whereas these compounds alter from open-chain into ring structures on going from alkylamino to methylthio substituted VII protonated species only exist in the cyclic structure.

Hitherto quantum-chemical studies have been mostly employed as a tool in interpreting UV/VIS and PE spectral data in order to provide a tentative or quite reliable assignment to one or the other isomeric species[9,29,40]. First attempts to predict favoured compounds in terms of calculated relative energies, however, were less successful. Results obtained by different quantum-chemical methods were inconsistent[44]. While EH (ref.[44]) and, according to more recent studies[45], ab initio calculations at the MP2 6-31G*//HF 3-21G[(*)] level favour the dithioglyoxal $(III'a)$ over the 1,2-dithiete $(IIIa)$ structure the inverse result was obtained by CNDO (ref.[44]), MNDO (refs[9,46]) and ab initio calculations at the STO-2G and STO-3G level[45,47]. The higher thermodynamic stability of $IIIa$ is only reflected, in principle, by the latter calculations. Early HMO calculations of compounds of the series $IIIa$ and $III'a$ predicted stabilization of the dithiete structure by acceptor substituents and stabilization of the dithione structure by donor substituents[48]. The isomeric compounds are lumomers because the MO correlation diagram of $IIIa/III'a$ by EHT displayed a crossing of the frontier orbitals. Since the relevant orbitals are of the σ- and π-type the number of π-electrons will alter upon ring opening or ring closure. The latter point has found more general attention more recently[49]. With regard to the correlation diagram the formally concerted thermal isomerization $IIIa \rightleftarrows III'a$ should be classified to Woodward-Hoffmann forbidden reactions[44]. Photochemical isomerization may be allowed, however.

In this paper we will present a detailed examination about valence isomeric non--charged dithio compounds of the series III (III') to VII (VII'). Our general aim is to compare structural features and relative stabilities of the various species at a uniform level of semiempirical theory (MNDO). In particular, we wish to elucidate trends in these properties in two specific areas (i) among compounds that differ in the substitution pattern and (ii) among compounds of different ring size. Another

point of interest is the path of thermal and photochemical isomerization and the nature of the transition structure involved.

THEORETICAL

The calculations were performed by the MNDO method of Dewar and Thiel[50]. The more recently derived optimum sulfur parameter set[51] was used instead of the formerly proposed one[52]. As demonstrated by calculated heats of formation and by calculated structural data the new parametrization of sulfur is preferable, in particular, for compounds with SS-bonds. However, as shown in a previous study of 30 conjugated organosulfur compounds the calculated lengths of the ―S―S―, =C―S and C=S bonds are still grossly underestimated[53]. Since the error is systematic, however, it can be accounted for by the following empirical correction: $R_{S-S} = 9$, $R_{C-S} = 6$, and $R_{C=S} = 3$ pm.

In general, MNDO geometry optimization was performed with allowance for independent optimization of all variables. The SCF convergence criterion was fixed to 10^{-7} eV. Along these lines bond lengths were optimized to 0·1 pm and bond angles to 0·1°. Force constants of the heterocyclic parent compounds *IIIa* to *VIIa* were also calculated to evidence that minima of the potential hyperface had been reached. In the case of open-chain compounds the MNDO calculations reflect a well known methodical deficiency: Conjugated open-chain compounds with essential single bonds are inclined to adopt a non-planar geometry in contradiction to experimental findings[53]. In order to avoid this pitfall geometry optimization of structures of the series *III'* to *VII'* were constrained to in-plane coordinates. These compounds as well as many derivatives of open-ring and closed-ring structures can be thought to exist in different conformations. Since we are exclusively concerned with the disulfide/ dithione isomerism open-chain compounds are generally considered only in its *s-cis* (or all-*cis*) structure which is transformed by a least motion single step into the cyclic counterpart. Disregarding any conformational equilibria the relative energy refers to the following geometries: The substituent groups NH_2 and CHO are assumed to be flat. The oxygen atom of CHO is positioned *syn* to the sulfur atom. Likewise, the dihedral angles of CH_3, CF_3, OCH_3, and SCH_3 were kept constant at standard values and the atoms of these groups were placed symmetrically relative to the molecular plane. The in-plane hydrogen (fluorine) atom was directed to the sulfur atom. Due to steric interference phenyl substituents depart somewhat from planarity. A twisting distortion of 43° taken from (Z)-stilbene[54] was pressumed in calculations of phenyl substituted compounds. The two phenyl groups were twisted in the disrotatory manner. As long as molecular crowding is avoided the question of the configuration chosen is of minor importance.

The barrier of isomerization between the cyclic structure and its non-cyclic congener was estimated by optimizing all in-plane variables except the distance between

the two sulfur atoms. In order to consider enhanced correlation energies associated with the bond-breaking process configurational mixing between the ground state and the doubly excited state was admitted (MNDO/2 × 2 CI procedure). Open shell structures such as the lowest-energy singlet and triplet excited state (S_1 and T_1, resp.) were calculated within the framework of the RHF half electron approximation (MNDO/HE). Based on this approximation a more adequate treatment of biradical species is afforded within the two-electron two-orbital model[55]. The resulting MNDO/HE/3 × 3 CI procedure was employed in the case of biradicalic dithio structures. The configurations chosen are defined by the frontier orbitals. The MNDO-LCI methods were designed by Dewar and coworkers and successfully used in treating problems of chemical reactivity[56].

In the basic conception of Dewar's MNDO method differences in energy between the isomers are identified with standard reaction enthalpies ΔH_{isom} of the respective equilibria. Correspondingly, differences in energy of the isomers and transition structures appear as enthalpies of activation. In this paper, ΔH_{isom} values are referred to the cyclic isomer. They are positive if the cyclic structure is favoured. Negative value indicate preference of the non-cyclic isomer.

RESULTS AND DISCUSSION

Some results of the calculations are collected in Table I. According to the calculated bond lengths all dithio compounds studied exist as isomers of the type A and A' rather than as any single species of the type A/A'. In view of this fact the former assumption of possibly existing "no bond resonance structures" must be rejected.

In one series, A, which encompasses heterocyclic compounds, a short distance between the sulfur atoms is obtained. Taking into account the additive increments mentioned above, R_{S-S} varies between 202 and 210 pm and R_{C-S} between 166 and 178 pm. In the other series, A', the distance between the sulfur atoms is relatively large (more than 280 pm) while R_{C-S} is short (157 to 161 pm). The latter compounds are non-cyclic dithiones. There are specific features in each class of compounds which are outlined in the following:

1,2-Dithietes

According to the data listed in Table I the parent 1,2-dithiete (*IIIa*) is by about 12 kcal/mol more stable than s-cis dithioglyoxal (*III'a*). A slightly lower value of about 9 kcal/mol has been obtained if the former parametrization of sulfur is used. An increase of the heats of isomerization occurs on passing from the parent compound *IIIa* to acceptor substituted dithietes (*IIIf, IIIo*, and *IIIq*) and on passing from *IIIa* to alkyl- (*IIIb, IIIc*) and to phenyl substituted dithietes (*IIIg*). Apart from *IIIg*, which has not been known so far, the predicted preference of the ring structure is in good harmony with the experiment. Likewise, the larger stability of

benzodithiete (*IIIr*) relative to *o*-dithiobenzoquinone (*III'r*) is fully borne by experimental findings mentioned above. According to the calculations the (corrected) bond lengths vary only slightly around 208 (S—S), 176 (C—S), and 138 pm (C=C) while the corresponding experimental data of the dithietes *IIIa*, *IIIf*, *IIIr* (X = S) and *IIIs* amount, on an average, to 209, 176 and 137 pm (cf. Table I, footnote *a*). Unfortunately, the experimental gas phase geometry of *IIIa* has not been obtained without certain assumptions. This prevents us from discussing the calculated structural data assembled in Fig. 1 in more detail. Relatively long CS bonds and short CC bonds of *III* do not indicate any aromatic bond delocalization that might be expected for the 6π electron system.

Donor substituents such as OMe or NH_2 reduce the heats of isomerization to a few kcal/mol. Experimental results mentioned above even suggest negative values. Whether the relative stability of the four-membered ring is generally overestimated by MNDO calculations cannot be answered with certainty. Strong solvent–solute interactions should be operative in the case of the polar thiocarbonyl isomers imparting these isomers a higher relative stability in solution. Even if solvent effects are neglected dithiooxamide (*III'i*) in its *s-trans* conformation is predicted to be more stable than the cyclic bisamino dithiete (cf. Table I, footnote *e*). This is in agreement with the experimental solid state structure[15]). The calculated destabilization of the open-chain structure by SMe groups is, however, at odds with the dimethyl tetrathiooxalate structure found experimentally in the gas phase[9] and in solution[19]. A more thorough theoretical and experimental study of the conformational mobility of *III'k* is required. It should only be mentioned that structural investigations on the thioxothioamide[57] *III'n* and on potassium tetrathiooxalate[58] revealed structures that are strongly distorted about the pivotal CC bond. The discrepancy between theoretical and experimental results is less severe when the more rigid bicyclic dithione *III'l* is considered instead of *III'k*. Due to the ring strain the calculated heat of isomerization of *IIIl*/*III'l* is strongly reduced. The acyclic structure *III'l* was verified experimentally[9].

According to Table I dithiones are characterized structurally by C=S bond lengths of about 161 pm (corrected average value) and relatively long C—C bonds, which connect the acceptor moieties (about 149 pm). Some additional calculations have revealed that open-chain structures of series *III'* are more stable in the transoid than in the cisoid conformation (such as *III'j* and *III'k*). However, the conformational mobility of dithiones is high enough to enable concerted $\left[{}_\pi 4_s + {}_\pi 2_s\right]$ cycloaddition reactions with dienophiles[59], which requires the cisoid conformer.

1,2-Dithiins

According to the heats of isomerization listed in Table I the six-membered 1,2--dithiin ring is clearly more stable relative to the open-chain counterpart than the

TABLE I

Selected bond lengths R^a, heats of formation $\Delta H_f^{\ b}$, first ionization energies IE^c and dipole of isomerization $\Delta H_{isom}^{\ b}$

Compound	R_{S-S} pm	R_{C-S} pm	$R_{C=C(X)}$ pm	R_{C-C} pm	ΔH_f kcal/mol	IE eV	μ D
IIIa	199	170	136	—	42·0	9·75	1·46
IIIb	198	170	137	—	17·2	9·53	1·55
IIIc	196	172	139	—	45·2	9·48	1·73
IIIf	199	169	138	—	−253·1	11·31	3·47
IIIg	198	171	137	—	85·2	8·82	2·11
IIIh	198	171	138	—	85·2	8·41	1·14
IIIi	199	171	138	—	49·8	7·68	2·61
IIIj	198	172	138	—	−37·3	8·68	0·42
IIIk	198	170	138	—	23·3	8·64	0·73
IIIl	201	168	138	—	78·0	8·84	1·01
IIIo	199	169	138	—	−24·6	10·36	0·94
IIIq	199	170	138	—	102·6	10·50	2·71
IIIr	200	169	144	—	47·7	9·08	2·02
IIIv^f	—	—	—	—	—	—	—
IVa	196	168	135	146	28·7	8·52	2·30
IVb	196	169	136	146	13·1	8·44	2·33
IVd	196	169	136	147	−256·8	9·72	2·17
IVe	195	169	136	146	82·4^g	8·28	2·24
IVf	195	170	137	145	41·0	7·59	1·34
IVg	195	170	137	145	−40·4	8·27	0·85
IVh	193	168	136	145	31·9	8·34	1·03
IVi	195	169	136	146	−29·8	9·11	0·86
IVj	196	169	136	146	96·4	9·31	2·09
IVk	196	169	136	146	134·8	8·38	2·40
IVl^h	195	169	140	151	56·6	8·86	2·60
IVn	194	169	138	148	152·6	9·09	6·64
Va	198	171	134	148	47·0	8·81	2·35
Vb	197	173	121	155	−44·0	10·35	0·92
Vc	198	170	154	150	68·9	9·73	0·35
VIa	195	164	136	145	87·9	6·97	2·18
VIc	195	164	158	144	83·0	7·80	5·96
VId	195	164	131	145	88·1	7·80	3·67
VIe	197	164	134	142	170·5	15·0	—
VIIa	195	163	124	146	32·7	8·41	4·39
VIIb	194	164	124	147	10·8	8·25	3·90
VIIe	194	165	124	147	79·3	7·79	2·97
VIIf	196	168	125	146	28·4	6·90	2·69

TABLE I

moments μ^d of cyclic disulfide (left part), their non-cyclic counterparts (right part), and heats

Com-pound	R_{S-S} pm	$R_{C=S}$ pm	R_{C-C} pm	$R_{C=C(X)}$ pm	ΔH_f kcal/mol	IE eV	μ D	ΔH_{isom} kcal/mol
$III'a$	337	155	147	--	53·7	9·60	2·22	11·7
$III'b$	312	156	149	---	42·4	9·47	2·89	25·2
$III'c$	275	157	154	--	96·7	8·71	3·13	51·5
$III'f$	302	156	149	- -	−221·5	10·82	3·42	31·6
$III'g$	301	157	150	---	115·9	9·09	4·04	30·7
$III'h$	301	157	150	--	116·2	8·80	3·69	31·0
$III'i^e$	317	158	151	—	53·0	9·06	6·37	3·2
$III'j$	319	157	152	--	−31·3	9·56	3·40	6·0
$III'k$	313	156	149	—	42·6	9·63	1·81	19·3
$III'l$	330	155	148	--	80·1	9·72	2·31	2·1
$III'o$	306	156	151	-·	7·4	9·99	1·04	32·0
$III'q$	320	156	150	...	124·7	10·52	2·26	22·1
$III'r$	318	156	150	.	78·6	9·19	3·48	30·9
$III'v$	283	154	151	- -	96·2	7·86	5·99	—
$IV'a$	317	155	146	136	70·7	8·91	3·38	42·0
$IV'b$	302	156	147	136	60·7	8·63	3·36	47·6
$IV'd$	295	156	146	136	−210·7	9·96	0·39	46·1
$IV'e$	299	156	147	136	129·4	8·48	3·62	47·0
$IV'f$	309	157	148	136	70·1	8·24	6·16	29·1
$IV'g$	306	157	148	136	−11·9	8·78	2·51	28·5
$IV'h$	304	156	147	136	59·2	8·86	0·89	27·3
$IV'i$	299	156	146	136	19·5	9·24	1·21	49·3
$IV'j$	304	156	147	136	141·3	9·61	0·97	44·9
$IV'k$	306	156	147	136	179·5	8·69	3·85	44·7
$IV'l$	294	157	147	141	136·3	7·99	4·01	79·7
$IV'n$	285	156	149	139	198·9	9·13	4·52	46·3
$V'a$	281	163	149	137	136·3	7·70	4·79	89·3
$V'b$	.-	—	—	--	---	--	---	—
$V'c$		---	—	-	---	. .	---	---
$VI'a$	321	155	148	136	72·6	8·89	4·31	− 15·3
$VI'c$	308	155	148	157	89·3	9·15	1·31	6·3
$VI'd$	322	154	149	130	80·3	9·24	2·17	−7·8
$VI'e$	327	155	148	130	212·2	14·28	—	41·7
$VII'a$	323	154	151	123	32·3	9·37	0·17	−0·4
$VII'b$	303	155	152	123	21·1	9·04	0·61	10·3
$VII'e$	295	156	153	123	94·2	8·78	1·56	14·9
$VII'f$	308	157	153	123	26·8	8·67	4·14	−1·6

TABLE I

(*Continued*)

Compound	R_{S-S} pm	R_{C-S} pm	$R_{C=C(X)}$ pm	R_{C-C} pm	ΔH_f kcal/mol	IE eV	μ D
VIIg	195	168	123	147	−44·8	7·54	5·45
VIIh	194	165	123	147	16·7	7·68	5·45
VIIj	194	164	122	148	−27·6	8·99	7·99
VIIk	194	164	123	148	95·1	9·20	6·12

[a] Experimental R values in pm: *IIIa* (MW, ref.[8]) S—S 209·6, C—S 175·3, *IIIf* (EB, ref.[5]) S—S 205, C—S 173, C=C 140; *IIIt* (X-ray, ref.[7]) S—S 212, C—S 177, C=C 139; *IVl* (X-ray, ref.[31]) S—S 205, C—S 175·7; *VIIe* (X-ray, ref.[42], average values) S—S 200·6, C—S 170·0, C—C 144·2.
[b] Energies in kcal/mol: 1 kcal/mol = 4·184 kJ/mol. [c] Experimental (vertical) IE values in eV: *IIIa* 9·05 (ref.[9]), *IIIb* 8·36 (ref.[9]), *IIIc* 9·75 (ref.[12]), *IIIf* 10·2 (ref.[9]), *IIIg* 10(?) (ref.[9]), *IIIr* 8·46 (ref.[11]), *III'k* (*s-trans*) 8·38 (ref.[9]), *III'l* 8·88 (ref.[9]). [d] Dipole moments in Debye: 1 Debye = = 3·3356 . 10^{-30} C m. Experimental dipole moments: *IIIa* 1·329 (ref.[8]), *VIIc* 3·50 (ref.[39]). [e] Theoretical results for *s-trans III'i*: $R_{C=S}$ = 158 pm, R_{C-C} = 151 pm, ΔH_f = 45·5 kcal/mol.
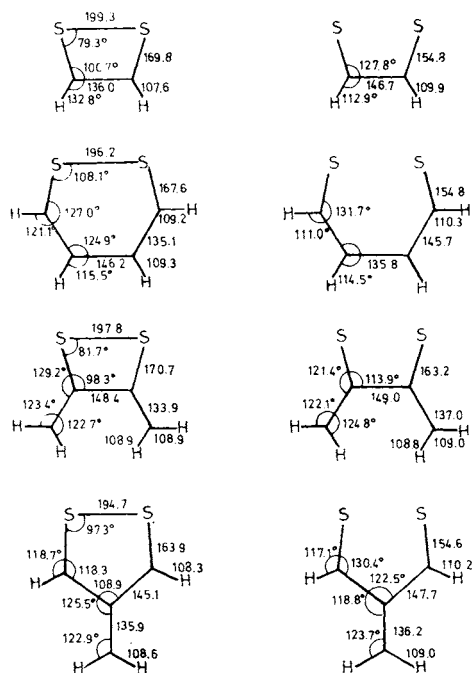

FIG. 1

Structural data of ring-closed disulfides and ring-opened dithiones obtained by geometry-optimized MNDO calculations

TABLE I

(Continued)

Com-pound	R_{S-S} pm	$R_{C=S}$ pm	R_{C-C} pm	$R_{C=C(X)}$ pm	ΔH_f kcal/mol	IE eV	μ D	ΔH_{isom} kcal/mol
$VII'g$	308	157	154	122	-52.8	9.17	0.64	-8.0
$VII'h$	299	155	153	123	25.2	9.09	1.11	8.5
$VII'j$	300	155	152	122	-15.1	9.56	3.94	12.5
$VII'k$	308	155	152	123	104.6	10.05	2.96	9.5

$IE = 9.23$ eV, $\mu = 0.0$ D; experimental R values in pm (X-ray, ref.[15], average of two equivalent molecules): 166 ($R_{C=S}$), 154 (R_{C-C}). ^{f} The dithiete structure is lost in favour of the valence isomeric dimethylene dithiane structure ($\Delta H_f = 133.8$ kcal/mol). The heat of isomerization with respect to $III'v$ amounts to -37.6 kcal/mol. ^{g} Experimental enthalpy of formation of IVe: $\Delta H_f = 101.1$ kcal/mol (ref.[67]). ^{h} The planar molecule ($\Delta H_f = 58.1$ kcal/mol) is 1.5 kcal/mol less stable than the distorted molecule IVl (calc. dihedral angle between phenyl groups 34.7°, exp. value 34.04°, see ref.[31]). Date of $IV'l$ also refer to the optimum distortion of the moieties (42.5°).

four-membered dithiete ring $(42.0$ kcal/mol versus 11.7 kcal/mol). Replacement of hydrogen atoms by CH_3 (IVb), CF_3 (IVd), Ph (IVe), CHO (IVi) or CN (IVj) in α-position of 1,2-dithiin brings about only a weak additional stabilization of the ring structure. Dithiins with acetylenic substituents such as IVk are also favoured over the corresponding dithiones supporting the structural assignment of natural dithio compounds to ring structures as already proposed in literature[60].

MNDO geometry optimization resulted in planar ground state molecules with a pronounced polyenic bond alternation along the perimeter (average values of 136 and 147 pm, resp.). The only exception among the compounds considered in this paper is dibenzo[c,e]dithiin (IVl). The potential curve of IVl, however, is flat with respect to the out-of-plane motion. The molecular planarity of the parent compound IVa is butressed by geometry-optimized STO-3G *ab initio* calculations $(R_{S-S} = 210, R_{C-S} = 176, R_{C=C} = 131,$ and $R_{C-C} = 149$ pm). It should be mentioned that results of corresponding MNDO and STO-3G calculations of the isomeric 1,4-dithiin are less consistent. MNDO calculations predicted a flattened molecule[53,61] whereas the STO-3G calculation resulted in a boat shaped geometry. The difference in energy, however, between the puckered and planar 1,4-dithiine is extremly small[61].

Donor substituted dithiins have lower heats of isomerization than the parent compound rendering equilibria of the dithiins with the corresponding dithiones more probable at room temperature in solution. Because of their highly polar groups dithiones will undergo marked solute–solvent interaction. The search for valence

isomeric 3,6-diamino-dithiins (dithiomaleinic amides) appears to be particularly promissing. Up to know only one representative of the isomeric dithiofumaric amide series has been described[38]. The formerly synthesized IVo (or $IV'o$)[34] has not been examined more closely.

Non-cyclic compounds of the series IV' are anticipated to exhibit a polyenic bond fixation. MNDO average bond lengths are 136 pm for the double bond and 147 pm for the single bond.

3,4-Dimethylene-1,2-dithiane, 4-Methylene-1,2-dithiole and Heteroanalogous Compounds

3,4-Dimethylene-1,2-dithiane (Va) and 4-methylene-1,2-dithiole (VIa) and their isomers constitute particularly intriguing cases because one of the two species (VIa) in each case, can only be formulated by a biradicalic structure.

According to the MNDO calculations the heterocyclic structure Va is highly favoured over $V'a$. The open chain structure $V'a$ displays a relative short SS-distance (280 pm) and double bonds are the CC rather than the CS bonds. However, the monoconfigurational description is no longer warranted in the case of the biradicaloid $V'a$. Calculations were repeated, therefore, with MNDO CI versions. In contrast to Va the 2×2 CI calculation of $V'a$ resulted in an appreciable singlet ground state depression (14 kcal/mol). Within the two-electron two-orbital model i.e. HE/3×3 CI calculation of the singlet and monoconfigurational HE calculation of the triplet state, the lowest energy singlet and the lowest energy triplet state have heats of formation of 96·4 and 95·8 kcal/mol, resp.* The triplet ground state of $V'a$ and the low $S-T$ splitting justifies a classification of $V'a$ to biradicaloid systems. More serious studies of $V'a$ with refined methods have to consider that the molecule may be twisted about the central CC-bond. The more stable cyclic valence isomer Va exhibits a strong bond fixation of the exocyclic methylene groups similar as known for radialene hydrocarbons (cf. Fig. 1). The same holds for the heteroanalogous derivatives Vb and Vc. They may be considered as inner dehydro products of the dithiooxalic and tetrathiooxalic acid, resp. None of the last compounds mentioned seems to be known so far.

4-Methylene-1,2-dithiole (VIa) deserves particular interest because this hydrocarbon represents the parent structure of compounds of the series VII. The cyclic structure VIa is less stable than the non-cyclic one $(VI'a)$. In contrast to series V, the cyclic structure is now the biradicalic one. The heat of formation of the ground state molecule (87·9 kcal/mol, cf. Table I) is lowered by 2×2 CI by 21 kcal/mol. The

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* The question arises to which extent such numerical predictions will be confident. Within the same approach the lowest energies of the singlet and triplet states of the biradicalic carbene differ in energy by 25·3 kcal/mol with the triplet being lower in energy. This is correct in principle, but the experimentally found ST splitting amounts to only 9 kcal/mol (ref.[62]).

heat of formation amounts to $71 \cdot 0$ kcal/mol if the singlet ground state is calculated by 3×3 CI. The triplet state is again the electronic state of the lowest energy ($\Delta H_f = 50 \cdot 3$ kcal/mol). Replacement of the exocyclic CH_2 group by the hetero-atoms O and S or by the heteroatomic groups NH and OH^+ imparts the cyclic structure growing stability relative to the corresponding open-chain structures. Despite the relative stabilization some derivatives such as 1,2-dithiol-4-one ($VIb = VIIa$) also belong to the biradicaloid structures. VIb is calculated to be most stable in the triplet state ($\Delta H_f = 11 \cdot 5$ kcal/mol). The same holds for VIc and VId. Protonation at oxygen, however, favours the singlet over the triplet molecule (VIe: $\Delta H_f = 170 \cdot 5$ kcal/mol for the singlet and $\Delta H_f = 186 \cdot 9$ kcal/mol for the triplet molecule).

Replacement of CH_2 of VIa by heteroatomic groups such as O will favour a zwit-terionic charge distribution of the singlet molecule. The charge separation, however, is lower than expected with the betainic dithiolylium-olate formula, which is widely used for the sake of simplicity. This is demonstrated in Fig. 2 with the molecular and electronic structure of VIb and some relevant data for comparative purposes. The same conclusion was reached by inspection of dipole moments[39]. The aromatic dithiolylium substructure, however, fully emerges with protonation at the oxygen atom on passing from VIb to VIe. The ring structure accounts for the experimentally observed tendency for ring closure of derivatives of the dithiomesoxalic acid in acidic solvents mentioned above.

1,2-Dithiolylium-4-olate

The perusal of the calculated heats of isomerization of $VII \rightleftarrows VII'$ shows that either the cyclic 1,2-dithiolylium-4-olates or their open-chain dithione counterparts are more stable and both of them may exist in equilibrium. Substituents such as Me, Ph, SMe, CHO or CN suffice to stabilize the cyclic over the non-cyclic structure. Because of the zwitterionic structure of VII mentioned above intermolecular interaction in polar solvents or in the crystal will additionally contribute to the relative stabilization of the cyclic structure. The low heats of isomerization calculated for bis(methylthio)--VII ($8 \cdot 5$ kcal/mol) does not contradict with the assumption[41] that the dithione isomer $VII'h$ may exist in equilibrium with $VIIh$ at elevated temperature to undergo $\left[_\pi 2_s + _\pi 4_s\right]$ cycloaddition with 1,3-dienes, whilst all remaining 1,2-dithiolylium-4--olates studied form 1,3-dipolar $\left[_\pi 4_s + _\pi 3_s\right]$ cycloadducts. However, inspite of efforts the equilibrium $VIIh \rightleftarrows VII'h$ could not be supported UV/VIS spectro-scopically[40].

The calculated molecular geometries of VII show average CS bond lengths at 171 pm (corrected value) and average CC and CO bond lengths at 147 and 123 pm, resp. Whereas the CS bond lengths fit quite well with experimental data reported for $VIIe$ and $VIII$ the CC bond lengths are too long and the CO bond length are too short by 2 to 3 pm. The error is not serious but may be already indicative for another

deficiency of the MNDO method consisting in an underestimation of bond delocalization in conjugated systems[63]. Some caution is also required in view of the fact that preliminary calculations[64] of vibrational frequencies did not provide the extremely low C—O stretching frequency found experimentally[40].

Open-chain structures are predicted with dialkyl dithiomesooxalates $(VII'g)$ and dithiomesoxalic diamide $(VII'f)$. Up to know compounds of the first series have not, been known. According to the MNDO calculations the average bond lengths R_{CS} R_{CC}, and R_{CO} are 161 (corrected value), 152, and 123 pm. The only experimental study offered with $VIIf$ (morpholino instead of NH_2) with corresponding bond lengths of 166, 151, and 121 pm is less suited for comparison. Due to steric congestion the molecule is heavily distorted.

Ionization Energies and Dipole Moments

Within Koopman's theorem the first ionization energy (IE) is related to the highest occupied MO from which one electron is ejected. This is a π-MO in the case of disulfide and an n-orbital in the case of dithione. In spite of the different origin of the ionization, the calculated first IE values of III and III' are in the same order of magnitude (cf. Table I). In the series IV and $VIII$ π-type ionization energies of the heterocycles are markedly lower than n-type ionization energies of the respective dithiones. In each series donor substituents reduce IE values while acceptor substituents enlarge them. The effect is only strong, however, for π-type ionization. The few experimental data available are about 0·8 eV* lower than the theoretical ones (vertical IE values; cf. footnote c to Table I). Thus the new parameter set of sulfur has brought about an appreciable reduction of the error (about 1·1 eV with the old parameter set). The differences between IE values, which are particularly informative
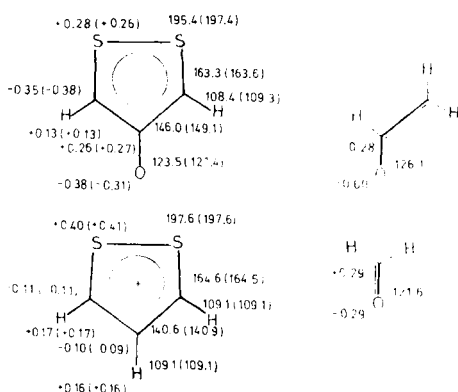

FIG. 2

Bond lengths (on the right) and net atomic charges of 1,2-dithiolylium-4-olate and selected data of dithiolylium, formaldehyde and vinyl alcoholate according to MNDO calculations (results of MNDO/2 × 2 CI calculations in parentheses)

*   1 eV = 1·602 . 10^{-19} J.

for structural analysis, are, however, practically not improved by reparametrization. The absolute average error between theory and experiment was estimated to 0·2 eV for the lowest three differences between IE values.

The dipole moments (μ) of cyclic disulfides are in general lower than those of acyclic thiones (cf. Table I). Some substituted compounds of series *VII* behave exceptionally due to the betainic charge distribution of the heterocycles. There is a shortage of experimental values. The few experimental dipole moments available are quite well reproduced theoretically (e.g. *IIIa* and *VIIc*, cf. exp. data in footnote *d* to Table I).

Valence Isomerization

The results of MNDO/2 × 2 CI calculations of *IIIa* (*III'a*) at different distances between the sulfur atoms are plotted in Fig. 3. The S_0 and S_2 potential curves display typical features of the avoided crossing of two electronic states of the same symmetry ($^1A_1$) resulting in a ground state barrier and a pericyclic minimum of the excited state curve. At distances between 251 and 252 pm the transition structure is traversed and the dithiete type structure turns to the dithione type structure. The barrier of the isomerization *IIIa* $\rightleftharpoons$ *III'a* amounts to about 36 kcal/mol relative to *IIIa* and 24 kcal/mol relative to *III'a*. The barrier is only slightly lowered if the symmetry of the transition structure is reduced from C_{2v} to C_2 by twisting the molecule about the S—S bond. Compared with experimental activation energies of electrocyclic reactions of hydrocarbons[65] the calculated barrier does hardly exceed
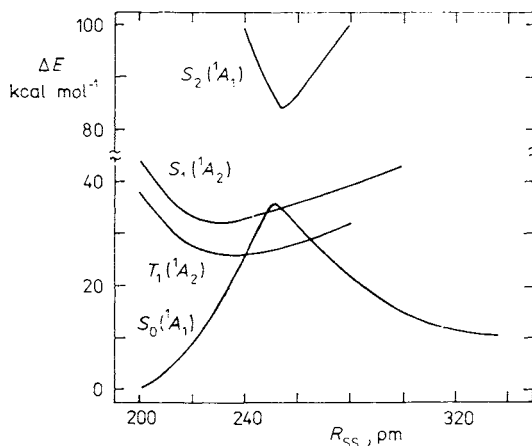

FIG. 3

Calculated energy variation along the assumed reaction path

that of Woodward–Hoffmann allowed reactions although the reaction considered above appears forbidden because of the symmetry-imposed orbital crossing. The experimental information is too scarce to know whether the calculated heat of isomerization and energy of activation of the dithiete dithioglyoxal system are theoretically underestimated or not. The experimentally determined[17] barrier of the derivatives $IIIh/III'h$ in solution amounts to about 20 kcal/mol. It is lower than that calculated for the parent compound.

The potential curves of the excited states S_1 $(^1A_2)$ and T_1 $(^3A_2)$, which are of the $\pi\sigma^*$ type for dithiete and $n\pi^*$ for dithioglyoxal, run through a minimum at 232 and 235 pm, resp. The curves intersect the ground state potential curve. According to former studies (Dewar and coworkers) the excited states are too low in energy with respect to the ground state[66]. A comparison between experimental excitation energies of $IIIa$ and $III'a$, which result from the maxima of UV/VIS absorption bands at 355 and 535 nm, resp.[20], and the (vertical) MNDO transition energies has shown that the S_1/S_0 energy gap is underestimated by 35 and 16 kcal mol, resp., at the MNDO optimum geometries of the two isomers. Irrespective of the accurate relative position of the potential curves their general features account well for the photochemical conversion of $IIIa$ into $III'a$ and vice versa. The S_1/S_0 surface touching or near surface touching will favour radiationless deactivation of the excited molecule through an appropriate funnel leading to the ground state of both valence isomers. The same conclusion is reached when the results of MNDO/HE 3 × 3 CI calculations are consulted. For reasons of symmetry the S_1 $(^1A_2)$ energy potential curve is not altered compared with that obtained from MNDO/HE calculations. The energies of the S_0 $(^1A_1)$ ground state are less negative but the nearly the same barrier is predicted as by MNDO/2 × 2 CI calculations (37 kcal/mol).

The study of the energetics of the ground and lowest-energy excited states of the parent 1,2-dithiin (IVa) has disclosed some similar features as found for 1,2-dithiete $(IIIa)$. According to MNDO/2 × 2 CI calculations the height of the barrier is below 50 kcal/mol relative to the more stable cyclic isomer and very small relative to the acyclic isomer assuming planar structures. In contrast to dithiete minima of the S_1 $(\pi\sigma^*)$ and T_1 $(\pi\sigma^*)$ potential curves are found at SS-distances closely similar to those derived for dithiin in the molecular ground state (about 210 pm). Thus photoexcitation to these excited states will not favour ring opening to the corresponding dithione. An early study[23] of the spectral pattern of IVa attributed its longwave absorption band at 451 nm to a $\pi \rightarrow \pi^*$ rather than $\pi \rightarrow \sigma^*$ transition[29]. Photochemistry of IVa cannot be well understood without a closer examination of different types of excited states and without consideration of competitive processes. Experimental results imply that 1,2-dithiins easily extrude sulfur[23,25] in forming thiophenes. The same reaction proceeds on exposure to UV or sun light[23,25,35].

According to preliminary MNDO/2 × 2 CI calculations of the isomers $VIIa/VII'a$ $(\Delta H_{isom} = 20.0$ kcal/mol in this approximation) at different SS-distances the ground

state barrier does not exceed 40 kcal/mol relative to the cyclic isomer. HOMO–LUMO excitation resulted in a $\pi\pi^*$ type excited state of *VIIa* and a $n\pi^*$ type excited state of *VII'a*. Because of the biradicalic nature of the parent compound *VII* theoretical studies on derivatives such as *VIIe* and *VIIh* may be more relevant. Thermal isomerization of *VIIh* appears to be feasible, but could not be confirmed so far by UV/VIS spectroscopy[40]. The photochemical reaction, on the other hand, seems not to result in valence isomerization. Irradiation of *VIIh* in solution ($CHCl_3$) causes reduction of the absorption bands of *VIIh* at 287 and 490 nm in favour of new absorption bands[40] at 339 and 409 nm (isosbestic point at 439 nm). The nature of the photoproduct has not been elucidated, hitherto.

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