Twist Angles and Bond Lengths in Three Twisted Push–Pull Ethylenes. Interplay between Steric and Electronic Effects

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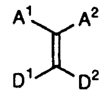
Crystal structures of 1,3-dibenzyl-2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hexahydropyrimidine and two of its sulfur derivatives have been determined by X-ray crystallography. The molecules are formally push–pull ethylenes, but due to strong steric interaction between the donor and acceptor parts they are twisted by 72° to 85° about the formal double bond, and they are best described as zwitterions with an amidinium ion and a carbanion part. The degree of twisting is discussed in terms of steric and electronic effects, and electron distributions from AM1 and CNDO/S calculations are described.

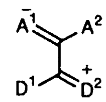
Previous studies[1–4] have shown that push–pull ethylenes (**1**, A^1 and A^2 are acceptor groups, D^1 and D^2 are donor groups) with the donor part consisting of two alkylamino groups joined in a five- or six-membered ring (**2**) are twisted about the $C^1{=}C^2$ bond. The degree of twisting depends on the steric interaction between the donor and acceptor groups but also on the respective donor and acceptor capacities of these groups. The energy of **1** as a function of the twist angle Θ can be discussed in terms of two contributions (Fig. 1). The first one, the π-electronic effect, E_π, has minima in the planar molecule ($\Theta = 0$ and 180°) and maxima when Θ is 90 and 270°. The difference $\Delta E_\pi = E_\pi(90°) - E_\pi(0°)$ is closely related to the barrier to hinder rotation about the $C^1{=}C^2$ bond in approximately planar push–pull ethylenes. It decreases with increasing the donor capacity of D^1/D^2 and with increasing the acceptor capacity of A^1/A^2. This should not be interpreted as a consequence of the greater weight of polar limiting structures like **1b**, although these contribute single bond character to the C(1)=C(2) bond. Great weight of **1b** also implies strong ground-state stabilization, which is barrier-raising. Instead, the reason for the lowered barriers has to be sought in an even greater stabilization of the transition state to rotation, which can be considered as a zwitterion composed of a carbocation, $(D^1\text{–C–}D^2)^+$, and a perpendicular carbanion, $(A^1\text{–C–}A^2)^-$, joined by a single bond.

The second energy contribution is the steric energy, E_{ster}, which has maxima at $\Theta = 0$ and 180° and minima at *ca.* 90 and 270°. The total energy, E_{tot}, is the sum of these two contributions, and the twist angle corresponding to the lowest total energy (Θ_{min}) depends on the relation between E_π and E_{ster}. Raising the E_{ster} curve while keeping E_π unchanged shifts Θ_{min} in the direction of 90 and 270°, while lowering E_{ster} under otherwise similar conditions changes Θ_{min} in the opposite direction. Two cases corresponding to $E_{\text{ster}} > E_\pi$ and $E_{\text{ster}} < E_\pi$ are shown in Figs. 1(*a*) and (*b*). The energy curves are simulated as Gaussians.

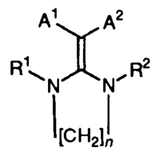
In order to study the effects on the geometry of twisted push–pull ethylenes of varying the steric and electronic effects of the substituents we have subjected compounds **3**, **4** and **5** to X-ray crystallographic studies. These compounds are well suited for an analysis of the steric and electronic effects, since they have important structural elements of rigid nature in common, in particular the donor parts, while at the same time crucial groups in the acceptor parts are different. The steric interaction



1a



1b



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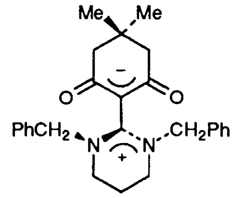

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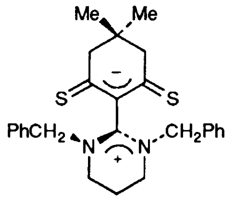

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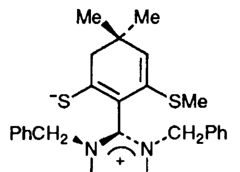
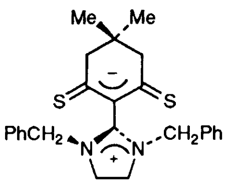
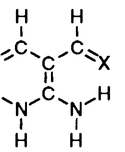


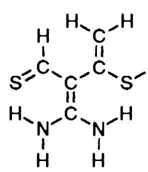
5



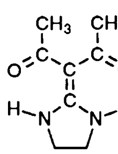
6



7 X = O
8 X = S



9



10

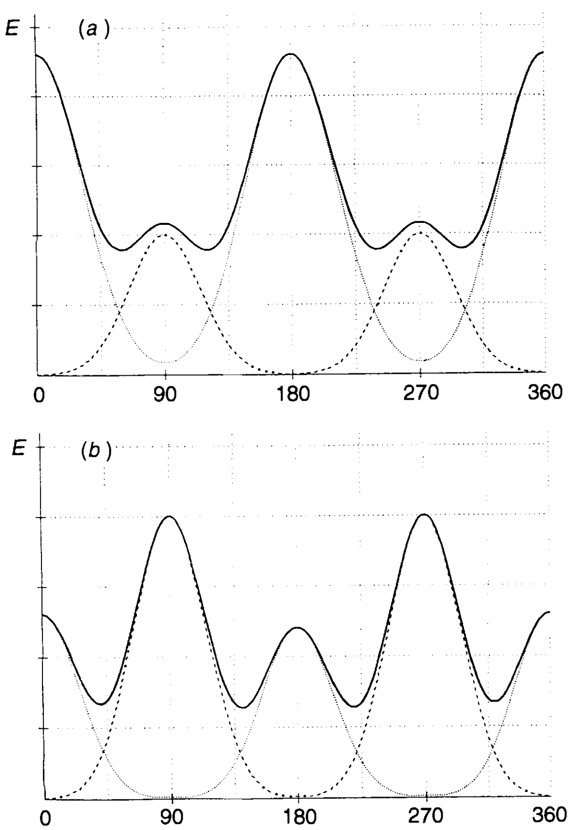


Fig. 1 Schematic curves of E_{ster}(······), E_π(------) and E_{tot}(——). (*a*) $E_{ster} > E_\pi$; (*b*) $E_{ster} < E_\pi$.

between donor and acceptor parts should follow the sequence **3** $\ll$ **5** < **4**. The difference between **3** and **4** is a consequence of the difference in size between C=O and C=S groups. This difference also explains the differences in barriers to racemization between chiral analogues of **3** and their mono- and di-thio derivatives,[5] and also the differences in barrier to isopropyl group rotation between 3-isopropylthiazolin-2-ones and their 2-thio derivatives,[6] and to rotation about the central bond in *N*,*N*,*N*′,*N*′-tetraalkyloxamides and their mono- and di-thio derivatives.[7] The difference in steric effect between **4** and **5** is probably small, but the larger steric effect of a C=S group conjugated with a donor group than of a C–S–CH_3 group has also been documented.[6] The explanation lies in the shorter C–S distance and in the higher electron density around the sulfur atom in the former case.

The crystal structures of the three compounds are rather similar. All are quite strongly twisted about the C(1)–C(2) bond, see Fig. 2, and the compounds are best described as betaines composed of an amidinium ion and a (thio)enolate ion.

The rings containing the nitrogen atoms in all three compounds and those containing the acceptor groups in **3** and **4** assume sofa conformations with five atoms nearly in one plane and the sixth, C(5), 0.62 to 0.67 Å out of the plane (Figs. 3 and 4). In **5** atoms C(2), C(3), C(6) and C(7) are practically in one plane with C(4) and C(5) slightly out of the plane in opposite directions (Fig. 5). Pertinent dihedral angles and bond lengths are found in Table 1.

Compound **4** has the largest twist angle, 85.1°, in agreement with the expectation that it has the highest E_{ster} and the lowest ΔE_π value. The two parts of the molecule are nearly perpendicular, but an even larger twist angle, 89.0°, has recently been reported for a sterically crowded 1,1-dinitro-2,2-diaminoethylene,[8] presumably due to a still lower ΔE_π value. The steric effect can be modulated by changing the size of the donor ring. It is larger with a six-membered than with a five-membered ring, as is illustrated by the analogue **6**, for which the twist angle is only 80.8°.[9]

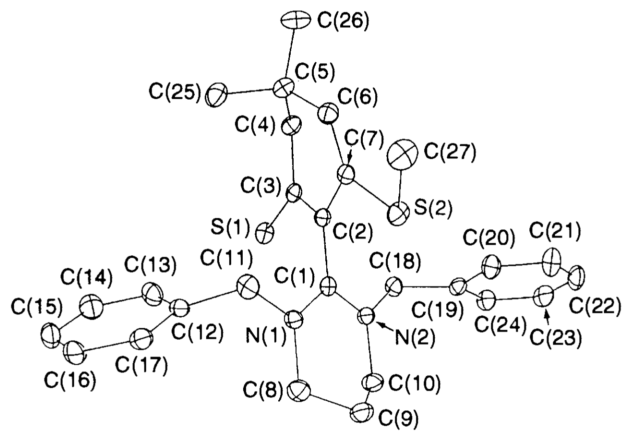


Fig. 2 Numbering of the non-hydrogen atoms in **5**. The same numbering is, *mutatis mutandis*, valid also for structures **3**, **4** and **7**–**9**.

Table 1 Selected dihedral angles (°) and bond lengths (pm) for compounds **3**–**5**[a]

	3	4	5
Angles			
N(1)–C(1)–C(2)–C(3)	79.7	85.8	71.0
N(2)–C(1)–C(2)–C(7)	78.0	86.1	74.3
Angle between N(1)–C(1)–N(2) and C(3)–C(2)–C(7) planes	78.8	85.1	72.5
Bond length			
C(1)–C(2)	147.2	146.6	147.6
C(1)–N(1)	131.6	131.6	133.8
C(1)–N(2)	134.3	132.1	133.8
C(2)–C(3)	136.9	141.4	137.3
C(2)–C(7)	143.9	140.4	149.7
X(1)–C(3)[b]	124.6	169.2	171.7
X(2)–C(7)	125.4	163.4	178.9
C(6)–C(7)			131.0
S(2)–C(27)			178.1

[a] For numbering, see Fig. 2. [b] X = O in **3**, X = S in **4** and **5**.

The lower twist angle for **3**, 78.8°, is in agreement with the expectation that this compound has a lower E_{ster} value than **4**. That the lowest twist angle, 72.5°, is found for **5**, in spite of a high E_{ster} value, must be explained by a quite high ΔE_π value for this compound.

The C(1)–C(2) bonds are very similar in length, *ca.* 147 pm, and the shortest bond goes with the largest twist angle (**4**) and *vice versa*. This is not as expected if conjugation effects alone are considered. The precision of the data does not allow a detailed discussion, but the fact that the longest bond is found in **5** may be interpreted by interplay between a strong steric effect and a high ΔE_π value. This leads to the largest strain, which is partly released by the largest stretching of the C(1)–C(2) bond.

In order to obtain an idea about the electronic energies and the electron distribution in **3**, **4** and **5** and their planar analogues, semiempirical quantum chemical calculations by the AM1 method have been performed on **7**, **8** and **9** with $\Theta = 0$ and 90° as simplified models of **3**, **4** and **5** devoid of steric effects. For comparison, data from CNDO/S calculations have been included. The results are shown in Table 2.

The calculated energy differences between planar and perpendicular models are not realistic. For **7**, the perpendicular form is even predicted to be more stable than the planar one by 21 kJ mol^{-1}, while experimental data show analogous com-

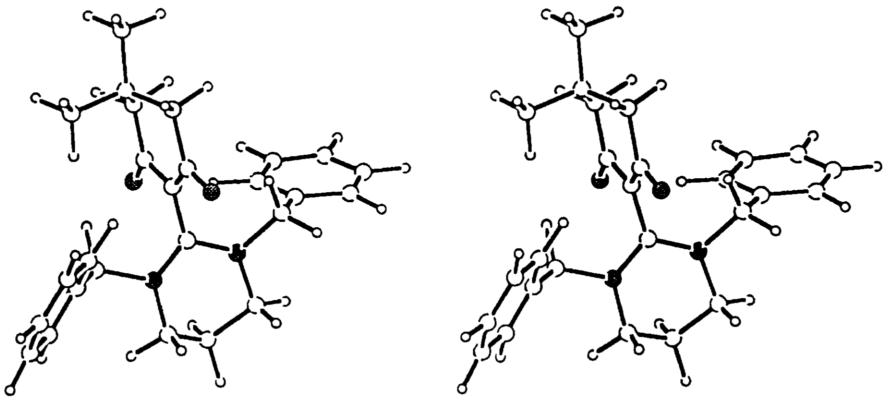


Fig. 3 Stereostructure of **3**

Table 2 Total energies (kJ mol^{-1}), formal charges (au) and bond lengths (pm) from AM1 calculations on the planar and 90° twisted structures **7**, **8** and **9**. Charges from CNDO/S calculations are included for comparison (italicized). The numbering of the atoms is as for **3**–**5**

			Charge								
Structure	Θ(°)	E_{tot}	X(1)	X(2)	N(1)	N(2)	C(1)	C(2)	C(3)	C(6)	C(7)
7	0	−159 047.0	−0.385	−0.385	−0.393	−0.393	+0.372	−0.519	+0.258	—	+0.258
			−0.382	*−0.382*	*−0.212*	*−0.212*	*+0.287*	*−0.135*	*+0.203*	—	*+0.203*
	90	−159 067.9	−0.411	−0.411	−0.334	−0.334	+0.449	−0.642	+0.263	—	+0.263
			−0.450	*−0.450*	*−0.104*	*−0.104*	*+0.372*	*−0.239*	*+0.186*	—	*+0.186*
		Δ*E* = −20.9									
8	0	−134 751.7	−0.179	−0.179	−0.382	−0.382	+0.339	−0.342	−0.091	—	−0.091
			−0.336	*−0.336*	*−0.241*	*−0.241*	*+0.289*	*−0.076*	*+0.128*	—	*+0.128*
	90	−134 704.2	−0.248	−0.248	−0.317	+0.421	+0.421	−0.424	−0.071	—	−0.071
			−0.439	*−0.439*	*−0.108*	*−0.108*	*+0.375*	*−0.135*	*+0.105*	—	*+0.105*
		Δ*E* = 47.4									
9	0	−149 714.5	−0.262	+0.018	−0.387	−0.393	+0.339	−0.290	−0.082	−0.292	−0.098
			−0.413	*−0.020*	*−0.219*	*−0.250*	*+0.280*	*−0.104*	*+0.108*	*−0.111*	*+0.053*
	90	−149 702.7	−0.415	+0.030	−0.318	−0.318	+0.420	−0.393	−0.043	−0.291	−0.100
			−0.541	*−0.084*	*−0.125*	*−0.125*	*+0.370*	*−0.161*	*+0.071*	*−0.126*	*+0.054*
		Δ*E* = 11.8									

		Bond length					
		C(1)–C(2)	C(1)–N(1)	C(2)–C(3)	C(2)–C(7)	C(3)–X(1)	C(6)–C(7)
7	0	143.1	137.3	144.4	144.4	124.4	—
	90	146.3	135.9	142.4	142.4	124.6	—
8	0	146.4	135.0	144.6	144.6	156.9	—
	90	148.9	135.3	140.3	140.3	157.0	—
9	0	145.3	137.5 136.6	141.1	146.0	158.9	134.5
	90	149.0	135.6	138.2	143.3	160.4	134.1

Table 3 Calculated dipole moments (D) for planar and perpendicular forms of **7**–**9**

Compound	Θ(°)	AM1	CNDO/S
7	0	4.14	1.20
	90	5.23	4.78
8	0	4.79	0.39
	90	5.25	3.06
9	0	5.66	6.37
	90	6.64	8.45

pounds to be planar in the absence of steric interactions.[2,8] The calculated Δ*E* value for **9** is also unrealistically low, albeit positive. The charges calculated by the two methods show notable differences, as do the corresponding dipole moments (Table 3). In particular, the C(1)–C(2) bond polarization is predicted to be much stronger by the AM1 than by the CNDO/S calculations, whereas the oxygen and sulfur atoms are given the largest electron densities by the latter method. In particular, it seems unrealistic that the negative charge on the sulfur atoms in **8** should be smaller than the corresponding charges on the oxygen atoms in **7**, as predicted by the AM1 but not by the CNDO/S calculations. C=S groups in general are much more polarized by donor substitutents than carbonyl groups[10] and this should be valid also for the vinylogous (dithio)carboxylate groups in **7** and **8**. Still, the general trends in the charge distributions and the changes in going from the planar to the perpendicular forms are rather similar in the two sets of calculations.

The calculated bond lengths appear fairly realistic, as do the changes predicted to occur on rotation from Θ = 0° to Θ = 90°. The C(1)–C(2) bond length in the nearly planar **10**, which has a conformation similar to that of planar **7**, is 144.2 pm,[2] to be compared with the predicted bond length of 143.1 pm. However, the predicted C–S bond lengths are all too short.

Experimental

Compounds.—The preparation of **3** and its bis-thionation to **4** have been described previously, as has the methylation-deprotonation of **4** to give **5**.[11]

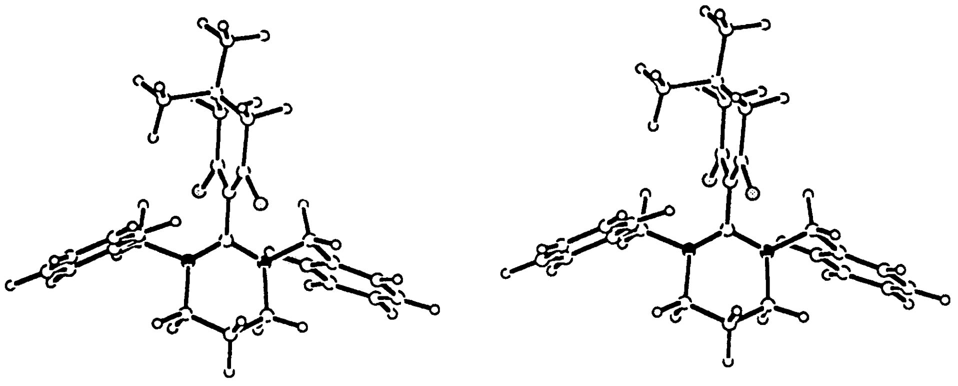


Fig. 4 Stereostructure of **4**

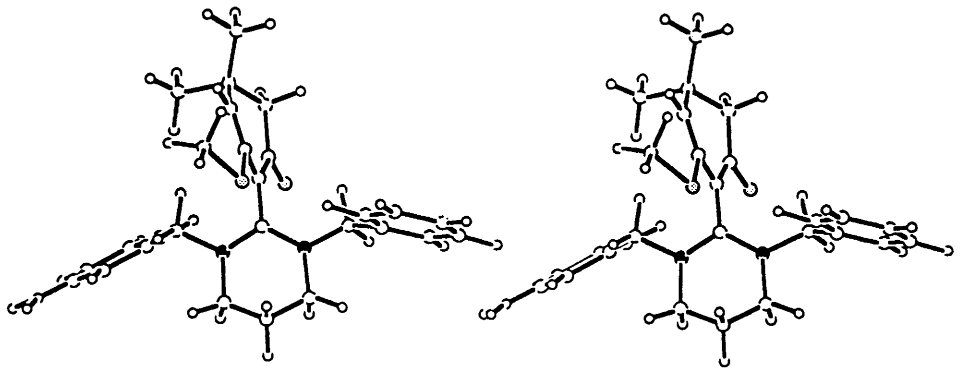


Fig. 5 Stereostructure of **5**

Table 4 Crystal data and intensity collection for **3–5**

	3	**4**	**5**
Empirical formula	$C_{26}H_{30}N_2O_2$	$C_{26}H_{30}N_2S_2$	$C_{27}H_{32}N_2S_2$
Colour, habit	White; chunk	Orange; thin needles	Orange; chunk
Crystal size/(mm)	0.24 × 0.10 × 0.08	0.01 × 0.02 × 0.24	0.24 × 0.30 × 0.68
Space group	*P*1; Triclinic	*Pbca*; Orthorhombic	*P*1; Triclinic
Unit cell:			
a/Å, α(°)	9.971(4); 88.90(3)	18.211(5); 90.00	9.225(3); 99.92(3)
b/Å, β(°)	10.113(3); 88.86(3)	10.372(4); 90.00	10.681(4); 94.45(3)
c/Å, γ(°)	11.297(4); 87.49(3)	25.146(8); 90.00	13.907(4); 113.16(3)
No. reflns. for indexing	11(8.25° $\le 2\theta \le$ 17.63°)	16(5.57° $\le 2\theta \le$ 18.40°)	15(10.46° $\le 2\theta \le$ 21.57°)
V/Å^3	1132.6(7)	4751(3)	1225.0(8)
M_w	402.5	434.6	448.7
D_c/Mg m^{-3}	1.180	1.215	1.216
Absorption coefficient	0.070	0.229	0.224
F(000)	432	1856	480
Diffractometer	Siemens R3 m/V		
Radiation	Mo-Kα (λ = 0.710 73 Å)		
T/K	297	296	297
Monochromator	Highly oriented graphite crystal		
2θ Range/°	2.5 to 45.0	2.0 to 40.8	3.0 to 50.0
Scan type	θ–2θ		
Scan speed (variable; ° min^{-1} in ω)	2.44 to 14.65	1.54 to 7.32	2.93 to 14.65
Scan range (°; plus Kα separation)	1.12	0.86	1.00
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25% of total scan time		
Standard reflections	3 measured every 50 reflections		
Index ranges	$0 \le h \le 10, -10 \le k \le 10, -12 \le l \le 12$	$0 \le h \le 17, 0 \le k \le 8, -24 \le l \le 0$	$0 \le h \le 9, -12 \le k \le 11, -16 \le l \le 16$
Reflections collected	3205[1078 > 3.0$\sigma(I)$]	2423[624 > 2.5$\sigma(I)$]	3963[2954 > 3.0$\sigma(I)$]
Independent reflections	2973[642 > 3.0$\sigma(I)$]	2036[549 > 2.5$\sigma(I)$]	3666[2445 > 3.0$\sigma(I)$]
Hydrogen atoms	Riding model, fixed isotropic U		Located from difference map
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0027F^2$	$w^{-1} = \sigma^2(F) + 0.0001F^2$	$w^{-1} = \sigma^2(F) + 0.0008F^2$
Number of parameters refined	74	141	408
Final R indices (obs. data, R; R_w)	0.0529; 0.0546	0.0699; 0.0559	0.0466; 0.0500
Goodness-of-fit	1.12	1.38	1.77
Largest and mean Δ/s	0.010; 0.001		0.072; 0.004
Data-to-parameter ratio	8.7:1	3.9 : 1	6.0:1
Largest difference peak/hole e Å^{-3}	0.40/−0.16	0.28/−0.29	0.29/−0.26

X-Ray Crystallography.—Unit cell parameters of compounds **3**–**5** were determined by a least-squares fit of 15 peak maxima with 2θ ranging from 5 to 22°. Three standard reflections, no intensity variation, 2973, 2576 and 3666 reflections were collected for **3**, **4** and **5** respectively. After Lorentz and polarization correction, 642 (**3**), 611 (**4**) and 2445 (**5**) unique reflections having intensities $I > 2.5\,\sigma(I)$ (**4**) or $I > 3\,\sigma(I)$ (**3** and **5**) were considered as observed and used in the structure analysis.

The space groups for **3** and **5** were determined as $P1$ based on the E-statistics: $|E^2\text{-}1| = 0.925$ (**3**) and 0.899 (**5**) and on the successful structure refinements. Based on systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$ and $hk0$, $h = 2n + 1$, the space group for **4** was determined as *Pbca*.

Detailed crystal data are listed in Table 4. The structures were solved by direct methods and successive Fourier syntheses. The full-matrix least-squares method based on F was used. The positions of hydrogens in **3** and **4** were all calculated and included in the final structure factor calculation. The positions of the hydrogen atoms in **5** were deduced from difference electron-density maps and were refined with an isotropic temperature factor. Scattering factors were taken from ref. 12. All calculations were performed on a DEC MicroVAX II computer system using the SHELXTL-Plus programs.[13]

Semiempirical calculations. The AM1 calculations were performed according to Dewar *et al.*[14] using the MOPAC program.[15] The CNDO/S calculations were performed with a program, specifically parametrized for sulfur compounds.[16]

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