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Structures of Linear Multisulfur Systems. X. Sulfur-Sulfur Bonding in Compounds with Four and Five Collinear Sulfur Atoms. A Discussion Based on MO-Calculations

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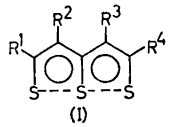
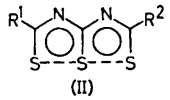
CNDO/2 calculations have been performed on a series of molecules containing four and five collinear sulfur atoms. The equilibrium geometries and charge distributions have been calculated. The theoretical results are compared with experimental data from X-ray crystallographic structure determinations. It is found that the CNDO/2 method is able to predict reasonably well in which cases partial bonding between sulfur atoms occurs. It is furthermore shown that the geometrical arrangements predicted for the sulfur sequences are closely related to those predicted for linear polyhalogen compounds.

It is well known that in structures of thiathiophthenes (I) and related compounds (*e.g.* II) the S–S bonds are found to be longer



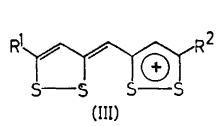
(I)



(II)

than corresponding single bonds.[1] Bonding schemes in which the central sulfur atom forms localized σ-bonds with the terminal sulfur atoms, utilizing *pd* or pd^2 hybrid orbitals, have been suggested.[2,3] Another of the proposed bonding schemes involves delocalized σ-bonding across the three sulfur atoms, 3-centre-4-electron bonding, in the following shortened 3c–4e bonding.[4,5] The description may be used with or without involving *d*-orbitals on the sulfur atoms. If *d*-orbitals are not included, this σ-bonding scheme is analogous to that suggested for trihalide ions by Hach and Rundle [6] and by Pimentel.[7]

Compounds including four and five collinear sulfur atoms, *e.g.* III and IV, may be described as extended thiathiophthenes. Several such



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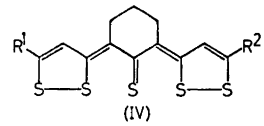


(IV)

compounds have been synthesized [8–11] and investigated by X-ray crystallographic methods.[12–23] In some of the compounds studied all S–S bonds have been found to be longer than single bonds, while in other compounds bond lengths comparable to those in five-membered cyclic dithioles are found.

The 3c-4e concept may be extended and generalized to give a description of *n*-centre bonds, (*nc-ve* bonds) as pointed out by Carpenter [24] and by Müller.[25] The general system under consideration by these authors is an array of *n* collinear equal atoms equally spaced. It is concluded that when $n \geqslant 4$, *n*-centre bonding is only to be expected if other forces keep the atoms in favourable positions.[25] In the higher homologues of thiathiophthenes, and related compounds, the carbon skeleton will tend to keep the sulfur atoms in favourable positions for delocalized *n*-centre σ-bonding.

In the present paper the results of CNDO/2 calculations on some selected model four- and five-sulfur compounds are given and compared with experimental results.

CALCULATIONS

The calculations have been performed with the CNDO/2 method, using standard parameters.[26–28] A slightly modified CNDO/2 program was employed.[29] *d*-Orbitals have not been included, due to the large number of additional parameters required in the calculations. Recent *ab initio* calculations give rather low *d*-orbital populations on the sulfur atoms in thiathiophthenes.[30] It is thus probable that the 3*d*-orbitals on sulfur in these compounds do not participate in building hybrid orbitals in the usual sense, but rather serve as polarizing functions on *s*- and *p*-orbitals so as to improve the occupied molecular orbitals without significantly changing their character.[31] On this background it seems reasonable to assume that the essential features of the bonding in the four- and five-sulfur compounds may be described by inclusion of only *s*- and *p*-orbitals.

It has been observed that CNDO/2 calculations with standard parameters and without *d*-orbitals predict too long S–S bonds in, *e.g.*, dithioles;[32,33] while calculations with *d*-orbitals yield too short S–S bonds.[32] Thus, when comparing experimental bond lengths with those predicted theoretically, the relative changes rather than the absolute values are relevant in the discussion.

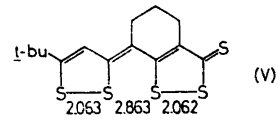
In the various model compounds studied by CNDO/2 the valence electron energy of the system has been calculated for different S–S bond lengths. The S–S distances have been varied by moving the sulfur atoms along the sulfur row, keeping other bond lengths and angles constant. This mode of calculation is somewhat artificial, as the geometry in general is affected when the S–S distances are changed. *E.g.* a C–S bond adjacent to a "short" S–S contact is invariably longer than a C–S bond adjacent to a "long" S–S contact. However, in calculating the energies for different S–S configurations, the effect of ignoring the overall geometrical changes will to a first approximation cancel when multi-centre and two-centre molecules are compared. If the synchronous changes in geometry should be fully taken into account, the amount of calculations required would be prohibitive.

If delocalized *n*-centre bonding is present in an *n*-centre system, all the bond distances along the array would be expected to be longer than a corresponding bond in a two-centre system. Therefore the equilibrium S–S distances arrived at for the four- and five-sulfur compounds, are compared with the corresponding distances calculated for closely related two-centre models, *i.e.* isolated five-membered cyclic disulfides.

RESULTS AND DISCUSSION

A. Four-sulfur compounds

1. *Model compound "a"*. The geometry as determined experimentally for compound V[14] was used as a basis for model "a" (Fig. 1).



(V)

The model was constructed exactly planar, hence the slight deviations in corresponding C–C and C–S bond lengths between V and "a". C–H bond lengths were set equal to 1.08 Å. The variation in energy for "a" as a function of the S3–S4 distance is plotted in Fig. 2. In the calculations S2 and S3 were moved symmetrically along the sulfur row, so as to leave S1–S2 equal to S3–S4. S–S distances corresponding to minimum energy

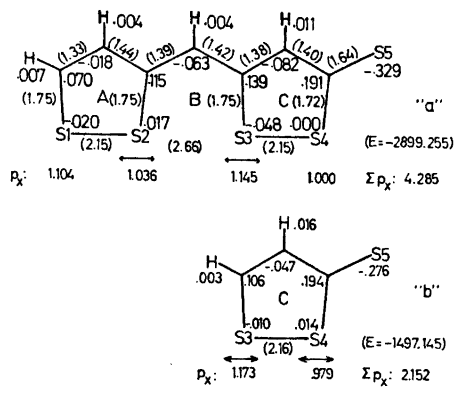


Fig. 1. Atomic charges and sulfur p_x population as calculated for models "a" and "b" at equilibrium geometries. Bond distances are shown in parentheses on "a". Bond lengths in "b" are as in ring C of "a". The minimum valence electron energies are given in units of eV.

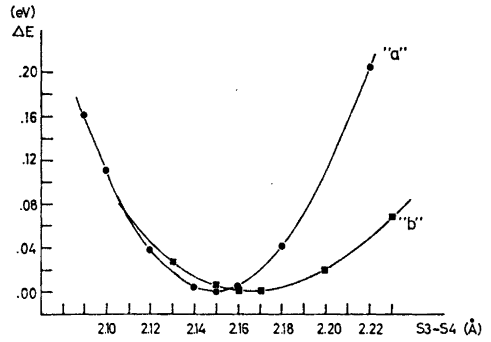


Fig. 2. The change ΔE in CNDO/2 valence electron energy for models "a" and "b" as a function of the S3–S4 bond length.

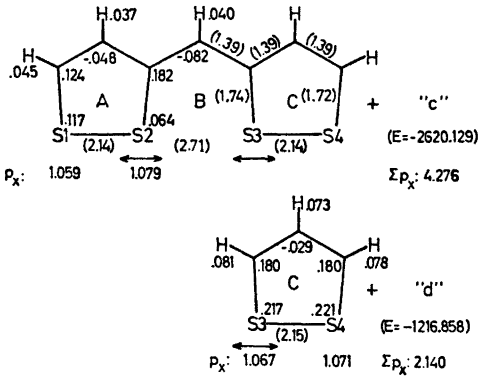
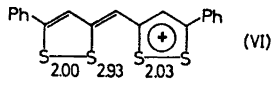


Fig. 3. Atomic charges, valence electron energy and sulfur p_x population as calculated for model compounds "c" and "d" at equilibrium geometries. Bond distances are given in parentheses on "c".

were derived by interpolation according to a second order polynomial fit. In order to compare the outer S–S bond distances arrived at in "a" with that in an isolated 1,2-dithiole ring of comparable geometry, calculations were carried out on 1,2-dithiole-3-thione (model "b").

In this calculation only one of the sulfur atoms, S3, was moved in order to mimic the calculations on "a". The optimized S–S distance in "b" is 2.16 Å while the outer distances in "a" are 2.15 Å. Hence, according to the CNDO results, the interaction between S2 and S3 does not lengthen the terminal S–S bonds in this four-sulfur compound relative to those of a dithiole. This is in agreement with experimental results which show the terminal distances in V to be of approximately the same lengths as the S–S bonds found in cyclic 1,2-dithioles.[14] According to the CNDO/2 calculations, both *s*- and *p*-orbitals are involved in the S–S σ-bonding; with *p*-orbitals giving the major contribution. Considering p_x-orbitals only as taking part in the S–S σ-bonding, there is a system with four centres and four electrons. The energetically most favourable arrangement apparently is two essentially localized 2c-2e bonds.

2. *Model compound "c".* The structure of the positive four-sulfur ion, VI, has been determined.[22] The outer S–S bond lengths determined experimentally do not differ significantly



from those of isolated 1,2-dithiolium ions.

For the calculations a model four-sulfur cation with twofold symmetry was constructed, model "c" (Fig. 3). As each of the outer rings in this molecule carries a formal charge of +0.5, it is not possible to find an exactly equivalent two-centre model for comparison. Instead a 1,2-dithiolium cation ("d") with geometry like ring C was used. The calculations give equilibrium S–S distances of 2.15 in "d" and 2.14 Å for the outer distances in "c". Both theoretical and experimental results thus suggest a bonding scheme in the four-sulfur cation equivalent to that in the neutral four-sulfur model "a".

3. *Model compound "e".* A negatively charged four-sulfur molecule has not yet been isolated. In such a compound there would be formally six p_x electrons in the sulfur array; *i.e.* a 4c-6e system. For the calculations on this anion an "unbiased" model "e" was constructed, with S–C = 1.72 Å, C–C = 1.39 Å, C–H = 1.08 Å, and bond angles at carbon atoms equal to 120°. S2 and S3 were moved as in the previous calculations. The equilibrium geometry arrived at is shown in Fig. 4. In this case the central S–S bond is the shorter one. The two-centre model used for comparison, model "f", is arrived at by a 180° rotation around each of the outer C–C bonds in "e". The optimum S–S bond length arrived at in the four-centre model is 0.04 Å longer than that in the two-centre

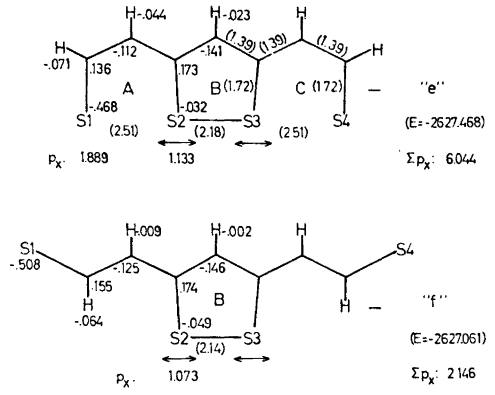
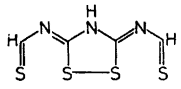


Fig. 4. Atomic charges, valence electron energy and sulfur p_x population as calculated for models "e" and "f" at equilibrium geometry. Bond lengths are shown in parentheses.

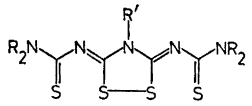
model. The calculations thus indicate that the interactions S1···S2 and S3···S4 are strong enough to have a lengthening effect on the central S–S bond, in agreement with the idea of σ-electron delocalization in electron-rich systems.

4. *Model compounds "g1", "g2" and "g3".* A neutral molecule isoelectronic to "e" is obtained by introducing nitrogen into the ring system in the manner illustrated in formula VII.



(VII)

Compounds analogous to VII have been synthesized,[10,11] and the structures of four of these have been determined by X-ray crystallographic methods.[19,20,23] The experimental results show that the central S–S bond is significantly longer than a single bond.



VIII (ref. 19)	2.763	2.167	2.763	R=i-pr, R'=Me
IX (ref.20)	2.745	2.196	2.676	R=i-pr, R'=p-NO_2-ph
	2.745	2.194	2.697	
	2.751	2.193	2.675	
X (ref.23)	2.742	2.161	2.785	R=Me, R'=Me
XI (ref.23)	2.784	2.171	2.784	R=Me, R'=ph

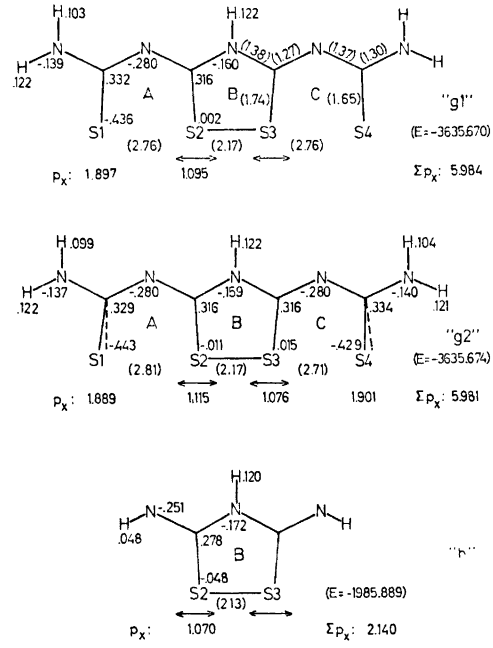


Fig. 5. Models "g1", "g2" and "h" with calculated atomic charges and sulfur p_x populations. N–H bonds = 1.04 Å, other bond distances are shown in parentheses.

CNDO/2 calculations were performed on a symmetrical model "g1" (Fig. 5). Optimal energy was found with the three S–S distances 2.76, 2.17 and 2.76 Å, respectively. The central distance is 0.04 Å longer than the S–S distance calculated for a reference cyclic disulfide, "h". Energy curves of the two models are shown

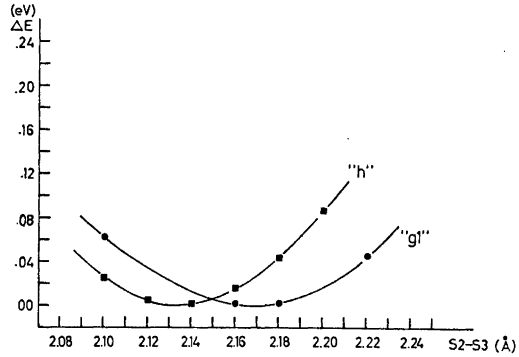


Fig. 6. The change ΔE in CNDO/2 valence energy for models "g1" and "h" as a function of the S2–S3 bond length.

in Fig. 6. As mentioned above the S–S bond lengths calculated by CNDO/2 for disulfides have been found to be approximately 0.1 Å longer than the experimental value. The calculated central S–S bond length in the four-sulfur model "g1" is, however, close to those observed experimentally in VIII–XI. The increase in S–S bond length by going from an isolated cyclic disulfide to the central ring of "g1" is hence underestimated in the calculations. Similarly, it has been found that CNDO/2 calculations not including *d*-orbitals on sulfur underestimate the variations in S–S bond lengths of open disulfides, R–S–S–R.[32]

The lengthening calculated for S2–S3 of "g1" is significant, and indicate that the three S–S bonds are partial bonds; as in the case of the four-sulfur anion (model "e"). As noted above, Müller has concluded that four-centre bonding is not very likely to occur.[25] Looking at Müller's energy calculations, however, it is seen that a four-centre bond has a significantly more favourable energy than a four-centre array with only *one* localized bond, while the energy difference between a four-centre bond and a system with *two* localized bonds, is minor.

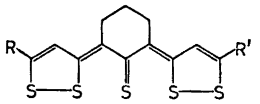
In compounds VIII and XI the sulfur sequences have two-fold symmetries due to crystallographic requirements. In IX and X, which are also symmetrically substituted, the sulfur arrays are unsymmetrical. This is probably caused by differences in the crystallographic environments of atoms S1 and S4. In IX each of the S4 atoms (there are three molecules per asymmetric unit) has a close contact to the molecular plane of a neighbouring molecule, while the S1 atoms have no such short contacts.[20] This indicates that the S–S bonds in these four-sulfur molecules are easily perturbed by weak intermolecular forces.

An unsymmetrical model "g2" (Fig. 5) was constructed by shifting S1 and S4 in model "g1" 0.05 Å along the sulfur row. Calculations were carried out, moving S2 and S3 as described earlier. A minimum energy, not significantly different from that of the symmetrical model, was obtained. The calculations show a small displacement of the atomic charges in "g2" compared to "g1". S1 and S2 carry slightly larger negative charges than S4 and S3, respectively. Such an electronic displacement might be introduced in IX, *e.g.* due to the relatively close contact of S4 to the π-electron cloud of a neighbouring molecule; and hence an asymmetric sulfur sequence would be favourable.

It is well known that in trihalides, with delocalized 3c-4e bonding, the X_3^- sequence is more asymmetric the longer the total $[X-X-X]^-$ sequence.[34] By analogy one would expect that in these 4c-6e systems a shorter S···S···S···S sequence would correspond to a longer central S–S bond. From the experimental results (VIII–XI) it is seen that the variations in the four compounds studied are small and not systematic. The short total S···S arrays in IX do, however, correspond to central S–S bonds which are significantly longer than those found in the three other compounds. CNDO/2 calculations predict a barely detectable lengthening of the central S–S bond when S1···S4 is shortened (from 2.168 Å in "g2" to 2.173 Å in "g3" where the S1···S4 sequence is shortened by 0.30 Å).

B. Five-sulfur compounds

5. Model compounds "i1" and "i2". The structures of three compounds, each with five approximately collinear sulfur atoms, have been determined by X-ray crystallography (XII, XIII, XIV).[12,16,21] Molecule XII which is unsymmetrically substituted, shows a slight asymmetry in the sulfur sequence. The symmetrically substituted molecule XIII has, within experimental error, twofold symmetry, while compound XIV which is also symmetrically substituted, shows a large deviation from symmetry in the sulfur sequence. In each compound all four S–S distances are significantly longer than S–S bonds in cyclic dithioles.



XII (ref.12)	2.14	2.62	2.55	2.16	R=ph, R'=t-bu
XIII (ref.16)	2.183	2.580	2.583	2.173	R=R'=t-bu
XIV (ref.21)	2.113	2.626	2.396	2.271	R=R'=p-MeO-ph

CNDO/2 calculations on a model with two-fold symmetry (model "i1") have been performed for various S···S distances (Fig. 7). The

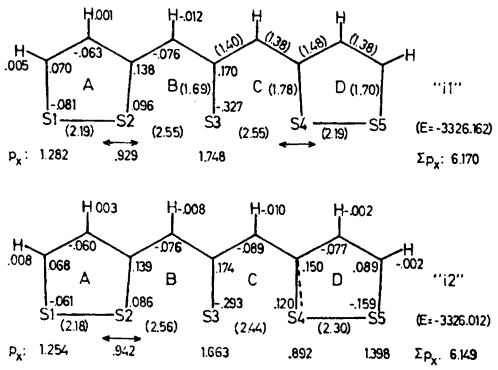


Fig. 7. Model compounds "i1" and "i2" with atomic charges and sulfur p_x population at equilibrium geometry. Bond distances are listed in parentheses.

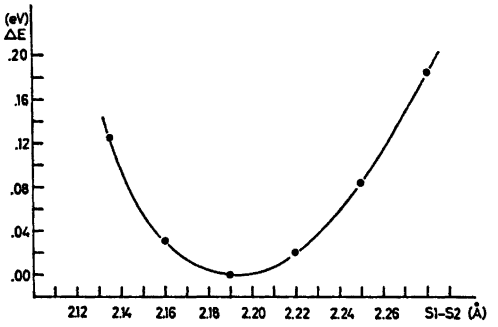


Fig. 8. ΔE plotted for model "i1" as a function of the S1 – S2 distance.

energy curve is plotted in Fig. 8. The results show that all S – S bonds are predicted to be longer than in dithioles; with the outer S – S bonds being the shorter ones, in good agreement with the experimental results. The calculated increase in S1 – S2 and S4 – S5 above the dithiole value, is, however, underestimated, as in the case of the four-sulfur compounds, "g1". In analogy with the notation used for the four-sulfur molecules, the partial bonding in the five-sulfur array may be described as 5c-6e bonding.

An unsymmetrical model "i2" was constructed by shifting S4 towards S3 such that S3 – S4 = 2.44 Å and S4 – S5 = 2.30 Å. In subsequent calculations these bond lengths were kept fixed, while moving S2. The CNDO results indicate that a lengthening of S4 – S5 will cause a slight shortening of S1 – S2. The experimental results show the same trend, however, much more pronounced (XIV).

As the two *p*-methoxyphenyl substituents in XIV have similar twist angles, the observed asymmetry in the sulfur array is probably induced by intermolecular forces. By studying the crystallographic packing it is found that the environments of the two outer disulfide rings are rather different. Dithiole ring A is sandwiched between the corresponding ring, A′, of another molecule and a phenyl group; while ring D's closest contacts are to a trimethylene bridge of another molecule.[21] It is possible that electronic repulsion between the π-electron clouds of ring A and its neighbours induces a migration of electronic charge from S1 towards S5. According to the calculations such an electronic displacement favours the asymmetric geometry observed where S1 – S2 is shorter than S4 – S5 (Fig. 7).

C. Models of polyhalides and polyhalogens

As mentioned in the introduction, the σ-bonding in thiathiophthenes apparently is similar to that in the trihalides. By analogy the σ-bonding in a linear X_4 (X = halogen)

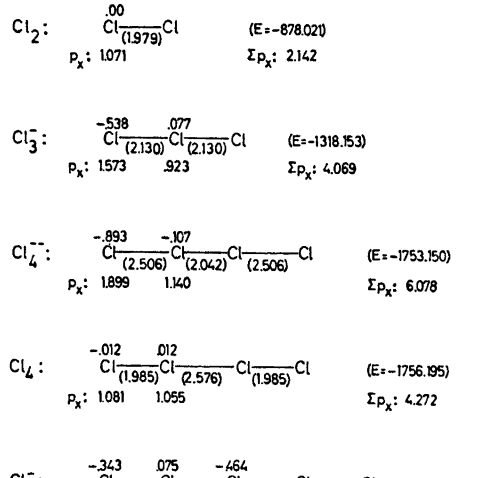


Fig. 9. Interatomic distances (in parentheses), atomic charges and p_x population in Cl_2,Cl_3^-, Cl_4^{2-}, Cl_4 and Cl_5^- at equilibrium geometries.

molecule might be of the 4c-4e type; while the bonding in X_4^{2-} and X_5^- may constitute delocalized 4c-6e and 5c-6e systems, respectively. In order to compare bonding patterns in the linear multisulfur compounds and linear polyhalogens, a series of CNDO/2 calculations were carried out on halogen model compounds. As the computer program available could not handle atoms with main quantum number larger than three, chloride compounds were used. Descriptions of the models and some results are summarized in Fig. 9. In the "free" Cl_2 molecule an interatomic distance of 1.978 Å is predicted by CNDO/2 in good agreement with the covalent single bond length of 1.98 Å.[35] Evidently the standard CNDO/2 parameterization gives a better fit for Cl_2 than for disulfides. The structure of a Cl_3^- ion is not known. Structures of Br_3^- and I_3^- ions, however, have been determined in several compounds (*e.g.* Refs. 36 – 39). Calculations were carried out for various Cl1···Cl3 distances. For each total length used, Cl2 was moved to find the lowest energy of the system. According to these calculations the optimal geometry of Cl_3^- is a symmetrical ion with Cl···Cl distances of 2.13 Å. For a symmetrical Cl_4^{2-} ion the calculations predict that all three bonds are significantly longer than a single bond. The equilibrium geometry is compatible to that of the sulfur arrays in models "e" and "g" suggesting a close similarity in bonding descriptions of these four-centre arrays.

The geometry of Cl_4^{2-} has not been determined experimentally. However, the homologous Br_4^{2-} ion has been observed in the crystal structure of W_6Br_{16}.[40] The ion is linear with a Br – Br distance of 2.43 Å for the central bond, and 2.98 Å for the two outer bonds. Similar four-centre arrays have been found in the compounds dimethylammonium bromide-bromine (2:1) and dimethylammonium chloride-iodine (2:1).[41] The average Br···Br distance of 2.8 Å is somewhat longer than that found in symmetrical Br_3^- (2.54 Å).[38] This is also in qualitative agreement with the average Cl···Cl distances of 2.35 and 2.13 Å predicted by CNDO/2 for Cl_4^{2-} and Cl_3^-, respectively. The halogen chains in the compounds mentioned above, have been interpreted as charge-transfer addition complexes formed by two halogen ions (donors) and one halogen molecule (acceptor).[42] The 4c-6e delocalized bonding concept describes the same system in terms of molecular orbital theory.

In a neutral four-centre model compound, Cl_4, CNDO/2 equilibrium geometry is calculated for a configuration with two short outer bonds and a long central distance. The outermost Cl – Cl bonds are almost identical to that predicted for Cl_2. This indicates that the σ-bonding in Cl_4 is equivalent to that in the four-sulfur array of model "a".

Calculations on a symmetrical linear Cl_5^- ion predict that all bonds will be longer than single bonds; – the outer bonds being the shorter ones, quite analogous to what has been found in the symmetrical five-sulfur sequences. X_5^- and YX_4^- halides known so far are nonlinear with two three-centre systems at right angles.[43,44] However, a linear polyiodide array has been recognized in a channel inclusion complex of trimesic acid polyiodide.[45]

CONCLUSION

CNDO/2 calculations have been performed on model compounds of linear multisulfur molecules, V – XIV. These calculations predict that relative to the S – S bond in an isolated cyclic disulfide, there will be a lengthening of S – S bonds in VII – XIV, but not in V and VI. This is in qualitative agreement with the experimental results.

Considering only p_x-orbitals as taking part in the S – S σ-bonding, a maximum of two *localized* S – S bonds may be formed both in a four-sulfur and a five-sulfur array. In four-sulfur compounds with four p_x-electrons, (V and VI), two localized S – S bonds are formed, while in four-sulfur compounds with six p_x-electrons, (VII-XI), there exists a delocalized 4c – 6e σ-bond. Analogously, in the five-centre compounds XII-XIV there exists a 5c – 6e bond. Thus, the results suggest that σ-delocalization occurs in these molecules when the number of p_x-electrons exceeds the number of atomic centres in the linear row.

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