Roesky's Ketone: Structure, Aromaticity and Reactivity

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The molecular and crystal structure of the title compound, 5-oxo-1,3,2,4-dithiadiazole or Roesky's ketone (**1**), is studied experimentally by re-determining the crystal structure and theoretically by calculations at the density functional level of theory using an extended basis set. A comprehensive set of properties, consisting of orbital topologies, atomic charges, atomic and molecular dipoles, aromaticity parameters and Fukui functions of the title compound and a number of its constitutional isomers was calculated in order to formulate a description of its structure, its aromaticity and reactivity.

Introduction

The discovery of the metallic properties of polymeric $(SN)_x$ in 1973,[1] and the finding that it becomes a superconductor at low temperatures two years later,[2] opened a new era in the research on conducting polymers. In $(SN)_x$ compounds the alternating sulfur and nitrogen atoms donate two π-electrons and one π-electron, respectively, which makes these compounds electron-rich and leads to a partial occupancy of the π*-orbital.[3,4] Such electron-rich compounds are known to be very reactive. One of the approaches to stabilize these interesting systems, and the one we adopted in this work, is to enclose chains of a limited length, for example an $(SN)_2$ unit, in a five- or six-membered ring, thus extending the π-delocalisation and stabilizing the heteroatomic fragment. The resulting new compounds have very different properties when compared with their hydrocarbon analogues. When, for example, naphthalene is compared with 1,3$\lambda^4\delta^2$,2,4-benzodithiazine, its analogue containing an $(SN)_2$ unit, we see that upon changing the −C=C−C=C− fragment into an −N=S=N−S− one the number of double bonds is retained but, in addition, one lone pair from the singly bound sulfur atom is introduced into the π-system. This causes 1,3$\lambda^4\delta^2$,2,4-benzodithiazine to become antiaromatic, while naphthalene itself is aromatic. These effects of electronic (de)localization, combined with the promising magnetic and electronic properties that result from the peculiar electronic structure, make these new compounds very interesting systems for further theoretical and experimental investigations.

Here we present an in-depth study of the structure, aromaticity and reactivity of one of these ring systems, in particular 5-oxo-1,3,2,4-dithiadiazole or Roesky's ketone, by combining the results from theoretical calculations and experimental techniques. A previous study on 1,3$\lambda^4\delta^2$,2,4-benzodithiazine and its fluorinated derivatives[5,6] provided a unique way to gain a deeper understanding of the properties of the molecule and to find out the best suited theoretical level to describe these properties, by comparing calculated geometries with the results of a gas-phase electron diffraction (GED) experiment. To complement the work presented here the influence of the theoretical level and basis set on the structure of Roesky's ketone was recently performed.[7] The small number of atoms makes this molecule especially interesting in such a study as we were able to use very high-level theories and very extended basis sets. Roesky's ketone can thus act as a model system for more complicated $(SN)_2$ systems. We are currently performing a similar study on an organometallic $(SN)_2$ compound containing a cobalt atom.

Roesky's ketone was first synthesised by Roesky and Wehner[8] in 1975 and later by Neidlein and Leinberger.[9,10] In 1978, the crystal structure of the ketone was determined by Roesky et al.[11] by means of X-ray diffraction (XRD). In 1993 deLaat et al.[12] studied Roesky's ketone in the gas phase by infrared (IR) and photoelectron spectroscopy (PES), and by a limited theoretical study using semi-empirical and low-level ab initio methods. In this work Roesky's ketone is subjected to a low-temperature X-ray diffraction study, yielding data with a higher resolution than the existing set. This experimental structural study is complemented by the calculation of a theoretical gas-phase geometry which is compared with the XRD results. A further descrip-

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tion of the molecular properties of Roesky's ketone is given based on calculated atomic charges, molecular and atomic dipoles, deformation densities, bond orders, Nucleus-Independent Chemical Shift (NICS) values, Fukui functions and softnesses, to gain a complete insight into the structure, reactivity and aromaticity of the title compound. To tackle the issue of aromaticity three constitutional isomers of Roesky's ketone, given in Figure 1, were included in the study.

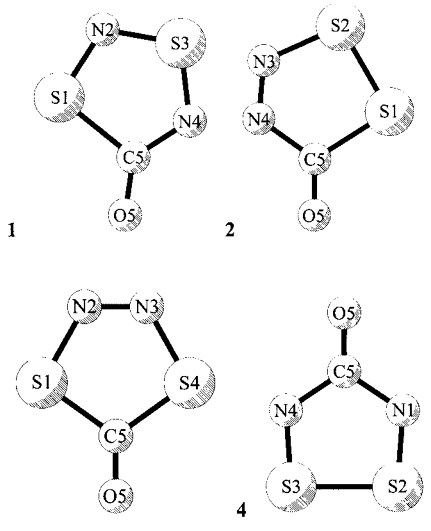

Figure 1. Molecular structure of Roesky's ketone (**1**) and its three constitutional isomers (see text for details); note that the numbering of the isomers is not systematic, but conforms to that of the parent compound for clarity

Results and Discussion

Experimental and Theoretical Geometry

The geometry of Roesky's ketone (**1**), which was synthesised as shown in Figure 2, was optimized at the DFT/B3LYP level of theory and the geometrical results are given in Table 1 together with the experimental solid-state geometry. The data show that the geometries of the two independent molecules in the unit cell are identical within the experimental errors; the torsion angles (not given in Table 1) are limited to 1.69(12)° and confirm the near-planar conformation of the compound in the solid state. This is in agreement with the planar conformation found in the calculations and suggests that the slight deformation in the crystal is due to packing effects. Keeping in mind that r_{XRD} are r_α-type distances which are compared to calculated (or r_e) distances, the agreement for the three N−S bonds is excellent for the longer one but less impressive for the two shorter ones, even though the relative bond lengths in the NSNS fragment are quite well reproduced. The difference between the calculated and the experimental bond length for the C−N and C−O bonds amounts to 0.02 Å; the calculation underestimates both. The only bond which is grossly overestimated by the DFT calculation is the C−S bond, with a difference of up to 0.11 Å compared to the experimental value. From a more systematic study of the influence of the level of theory, the functional used in DFT and the basis set on the calculated structure of Roesky's ketone, the results of which can be found elsewhere,[7] it is clear that B3LYP/6-311+G* leads to a high-quality structure in a relatively short computational time.

Table 1. Molecular geometry (r_e in Å and angles in °) calculated for 5-oxo-1,3,2,4-dithiadiazole (**1**) at the DFT/B3LYP/6-311+G* level of theory, and the experimental solid-state geometrical data (distances in Å and angles in °) for the two independent molecules in the asymmetric unit

	DFT	XRD	
S1−N2	1.6408	1.6395(14)	1.6425(15)
N2−S3	1.6083	1.5807(15)	1.5814(15)
S3−N4	1.5953	1.5763(15)	1.5750(16)
N4−C5	1.3650	1.386(2)	1.384(2)
C5−S1	1.9410	1.8305(17)	1.8293(16)
O5−C5	1.1939	1.211(2)	1.211(2)
S1−N2−S3	112.37	112.37(9)	112.04(8)
N2−S3−N4	106.78	106.13(7)	106.24(7)
S3−N4−C5	116.31	114.60(11)	114.74(11)
N4−C5−S1	107.86	109.73(11)	109.63(12)
C5−S1−N2	96.68	97.17(8)	97.32(8)
O5−C5−S1	120.82	123.79(13)	123.72(12)
O5−C5−N4	131.32	126.49(15)	126.65(15)

5-Oxo-1,3,2,4-dithiadiazole (**1**) is a five-membered-ring structure which is characterised by one longer (1.641 Å) and two shorter (av. 1.579 Å) S−N bonds, a regular-length C−N bond (1.385 Å), a longer C−S bond (1.830 Å) and a localised C=O double bond (1.211 Å). The internal angles of the ring are all centred around 110°, which is close to the ideal value of 108° for a regular pentagon, apart from the C5−S1−N2 angle, which severely distorts the structure, as can be seen in Figure 1. Figure 3 shows the crystal structure and packing of the title compound: the orthorhombic unit consists of 16 molecules (two in the asymmetric unit) packed in a parallel configuration, which are slightly distorted from the planar conformation.

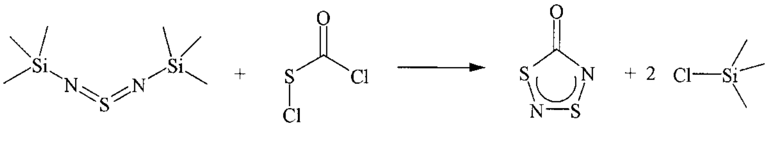

Figure 2. Synthetic pathway to 5-oxo-1,3,2,4-dithiadiazole (**1**)

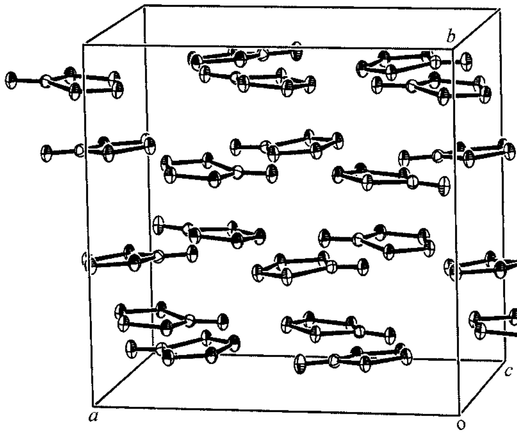

Figure 3. Crystal structure and packing of Roesky's ketone (**1**)

Frontier Orbitals and Geometries of the Anion and Cation

In Figure 4 the frontier orbitals are visualized using the program gOpenMol[13,14] for values of the contour surfaces of −0.035 and 0.035. Based on these pictures, the geometries of the anionic and cationic forms of Roesky's ketone can be rationalized. The geometries of the anion and the cation and the differences with the neutral molecule are given in Table 2. Based on the nodes of the HOMO, it is to be expected that the C5−S1, N4−C5 and N2−S3 bonds are longer in the cation than in the neutral molecule, as the HOMO has bonding character on these bonds: upon removing an electron from that orbital, the bonding will decrease, resulting in the lengthening of the bonds. This is indeed observed, as can be seen from Table 2: an increase in interatomic distance of up to 0.077 Å is found for the N2−S3 bond. The same reasoning can be applied for the three remaining bonds, which all become shorter. The removal of an electron from an orbital with anti-bonding character (the nodes in Figure 4a) will increase the bonding and shorten the bonds. Similar conclusions can be drawn for the anion, taking into account that here an extra electron is introduced into the LUMO. The bond lengths of the bonds where this orbital has anti-bonding character — all of them except N4−C5 — will increase, since the anti-bonding character is further increased. The bond length corresponding to the one bond in which there is bonding character (N4−C5) will decrease. All these trends can be found in the calculated geometry differences, given in Table 2.

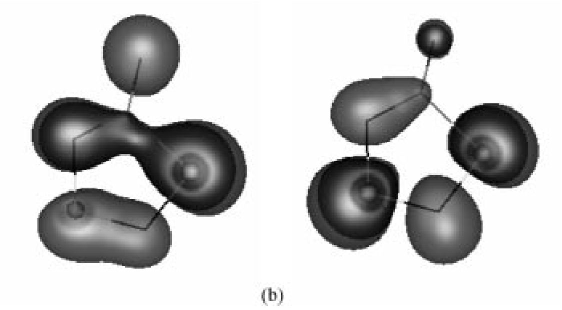

Figure 4. (a) HOMO and (b) LUMO of 5-oxo-1,3,2,4-dithiadiazole (**1**); see text for details

Table 2. Geometries of neutral 5-oxo-1,3,2,4-dithiadiazole (**1**), its cationic and anionic forms and the differences Δ (= $r_{\text{ion}} - r_{\text{neutral}}$); bond lengths are given in Å and angles in °

	Cation	Δ	Neutral	Anion	Δ
S1−N2	1.5797	−0.0611	1.6408	1.6834	0.0426
N2−S3	1.6852	0.0769	1.6083	1.7052	0.0969
S3−N4	1.5749	−0.0204	1.5953	1.6794	0.0841
N4−C5	1.3792	0.0142	1.3650	1.3156	−0.0494
C5−S1	2.0018	0.0608	1.9410	1.9618	0.0208
O5−C5	1.1808	−0.0131	1.1939	1.2236	0.0297
S1−N2−S3	115.02	2.65	112.37	109.38	−2.99
N2−S3−N4	104.50	−2.29	106.78	105.35	−1.44
S3−N4−C5	117.58	1.27	116.31	116.91	0.61
N4−C5−S1	107.37	−0.48	107.86	109.90	2.04
C5−S1−N2	95.53	−1.15	96.68	98.46	1.78
O5−C5−S1	121.39	0.57	120.82	117.25	−3.57
O5−C5−N4	131.23	−0.09	131.32	132.85	1.53

Charges and Dipoles

As the Hirshfeld partitioning of the electron density is an excellent way to attribute charges to atomic centers, stockholder charges, which are calculated according to this scheme, are known to be chemically very acceptable.[15−18] Stockholder charges were therefore calculated for the neutral 5-oxo-1,3,2,4-dithiadiazole (**1**) and for both its cation and anion; the obtained values are given in Table 3. Several features which are based on chemical knowledge, such as the dipole in the carbonyl group, the positive charges on the sulfur atoms and the negative charges on the nitrogen atoms, are reproduced well. The charges of the ionic forms of **1** will be used later in the reactivity discussion.

Table 3. Stockholder charges (in |e|) of neutral 5-oxo-1,3,2,4-dithiadiazole (**1**), its cationic and anionic forms and the differences Δ (= $q_{\text{ion}} - q_{\text{neutral}}$)

	Cation	Δ	Neutral	Anion	Δ
S1	0.435	0.291	0.144	−0.112	−0.257
N2	−0.056	0.100	−0.155	−0.281	−0.126
S3	0.520	0.203	0.318	−0.013	−0.330
N4	−0.042	0.143	−0.185	−0.280	−0.095
C5	0.196	0.068	0.128	0.065	−0.063
O5	−0.054	0.196	−0.250	−0.379	−0.129

The molecular dipole moment, μ, was calculated to be 3.104 D and its components are $\mu_x = -0.259$ D and $\mu_y = -3.093$ D, in the axis system given in Figure 5. The nth component of the molecular dipole, μ_n, with $n = x, y, z$, can be written as

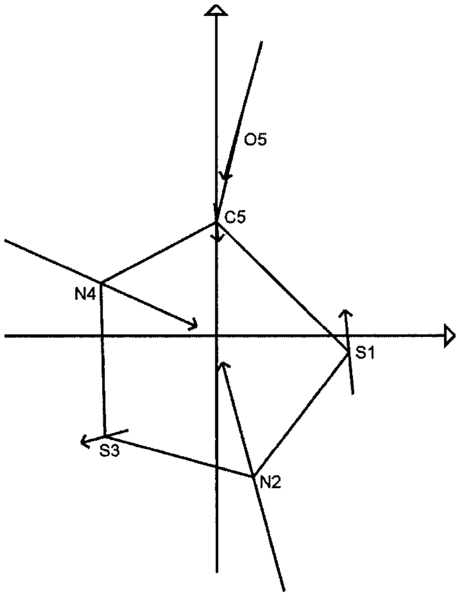

Figure 5. Atomic dipole moments in the Cartesian frame of the calculation; the size of the atomic dipole moment vector arrows has been increased by a factor of 100

$$\mu_n = \sum_A q_A R_{A,n} + \sum_A \mu_{A,n}$$

which is the sum of the contributions of charge transfer (first term, with q_A the stockholder charge and $R_{A,n}$ the coordinate of atom A) and of the intra-atomic charge polarization, calculated by the atomic dipole moment components $\mu_{A,n}$ (second term). Table 4 compiles these components for all six atoms in Roesky's ketone. It is clear that the contributions of the atomic dipoles, represented by the arrows in Figure 5, can be summed over the whole molecule to a net dipole with components of about 0.1 D in both the x and y directions. On the other hand, the charge-transfer contributions of the five ring atoms can be summed to a net zero charge transfer, indicating that the total charge transfer is determined solely by the value of the oxygen atom. Since the absolute values of the components of the total charge transfer outweigh those of the total atomic dipole, it can be said that the charge transfer of the oxygen atom indirectly determines the total molecular dipole moment. This is indeed found when the components of the charge transfer contribution of the oxygen atom (−0.336 and −2.819 in the x and y directions, respectively) are compared to the components of the total molecular dipole moment (−0.259 and −3.093 D in the x and y directions, respectively).

Table 4. Components, $\mu_{A,n}$, of the atomic dipole moment vectors, μ_A, and components, $q_A.R_{A,n}$, of the atomic charge transfers, in D, calculated for Roesky's ketone (**1**)

	$\mu_{A,x}$	$\mu_{A,y}$	$\mu_{A,z}$	$q_A.R_{A,x}$	$q_A.R_{A,y}$	$q_A.R_{A,z}$
S(1)	−0.020	0.224	0.000	0.963	−0.120	0.000
N(2)	−0.163	0.608	0.000	−0.287	1.096	0.000
S(3)	−0.125	−0.033	0.000	−1.782	−1.594	0.000
N(4)	0.508	−0.229	0.000	1.073	−0.488	0.000
C(5)	0.010	−0.102	0.000	0.000	0.730	0.000
O(5)	−0.102	−0.366	0.000	−0.336	−2.819	0.000
Sum	0.109	0.102	0.000	−0.369	−3.195	0.000

Aromaticity

Aromaticity remains a very complicated and debated issue in the whole of chemistry. Particularly in the field of computational chemistry, many researchers have tried to formulate unambiguous criteria for this elusive property during the past few decades; for a comprehensive work on aromaticity we refer to the book by Minkin, Glukhovstev and Simkin.[19] It is known that aromaticity involves the cyclic electron delocalisation coupled with an energetic stabilization, but the underlying physical nature of this aromatic stabilization is not known. An extensive set of criteria, which can be grouped into structural, energetic and magnetic criteria, can be found in literature, but it is believed that none of them alone can lead to an unambiguous definition of aromaticity. For this reason, an attempt is made in this work to combine a structural, an energetic and a magnetic criterion in order to ascertain whether the title compound is aromatic, anti-aromatic or nonaromatic.

In the first instance an attempt was made to qualitatively describe the influence on the aromaticity of the fragment closing the heterocyclic NSNS ring using structural and magnetic criteria. For a benzene ring as the closing fragment it was found in the gas-phase electron diffraction (GED) study[5] of 1,3$\lambda^2\delta^4$,2,4-benzodithiadiazine that the heterocycle features one localized single S−N bond [1.697(5) Å] and two localized S=N double bonds [1.548(3) and 1.543(3) Å]; this trend was confirmed by a B3LYP/6-311+G* calculation yielding 1.717, 1.570 and 1.566 Å as the bond lengths, respectively. This geometrical data, together with a calculated NICS value of 14.99 ppm at the B3LYP/6-31+G* level,[6] indicates that the heterocyclic ring is anti-aromatic; a positive value indicates anti-aromaticity, a value approximating zero nonaromaticity and a negative value aromaticity. For 5-oxo-1,3,2,4-dithiadiazole (**1**), where the ring is closed by a carbonyl group, we find more intermediate bond lengths of 1.641, 1.608 and 1.595 Å, which suggest a higher degree of electron delocalisation and thus a higher degree of aromaticity. The NICS value of −11.13 ppm confirms the suggestion that the molecule is aromatic. Other structural criteria also express this electron delocalisation. Table 5 presents the calculated bond orders of Roesky's ketone (**1**), which can be conveniently combined with a graphical representation of the electron delocalisation in the form of a deformation electron density. For Roesky's ketone (**1**) the latter is plotted in Figure 6 through the molecular plane. It is clear from Figure 6 that the bond-order values can be correlated with the peak heights on the bonds in the deformation map: the three N−S bonds have similar bond orders (0.94, 1.23 and 0.98) and produce peaks of similar height in the density map, indicative of electron delocalisation. The C−N bond is somewhat stronger (1.33)

Table 5. Selected geometrical data (r_e in Å and angles in °), bond orders (BO), total energies E (in H) and NICS values (in ppm) in the plane of the molecule [at the ring center, NICS(0)] and at 1 Å above the ring center [NICS(1)] of Roesky's ketone (**1**) and its constitutional isomers **2**−**4**

1		BO	**2**		BO	**3**		BO	**4**		BO
S1−N2	1.6408	0.94	S1−S2	2.0630	1.02	S1−N2	1.7423	0.67	N1−S2	1.5718	0.97
N2−S3	1.6083	1.23	S2−N3	1.7638	0.70	N2−N3	1.2376	2.07	S2−S3	2.1493	0.91
S3−N4	1.5953	0.98	N3−N4	1.2272	1.92	N3−S4	1.7423	0.67	S3−N4	1.5718	0.97
N4−C5	1.3650	1.33	N4−C5	1.4542	0.86	S4−C5	1.8121	0.87	N4−C5	1.4283	1.25
C5−S1	1.9410	0.74	C5−S1	1.8519	0.92	C5−S1	1.8121	0.87	C5−N1	1.4283	1.25
O5−C5	1.1939	1.94	O5−C5	1.1861	1.98	O5−C5	1.1939	2.08	O5−C5	1.1997	1.90
NICS(0)	−11.13		NICS(0)	−14.02		NICS(0)	−3.46		NICS(0)	−18.01	
NICS(1)	−7.73		NICS(1)	−9.54		NICS(1)	−4.17		NICS(1)	−11.88	
E	−1019.266		E	−1019.278		E	−1019.270		E	−1019.249	

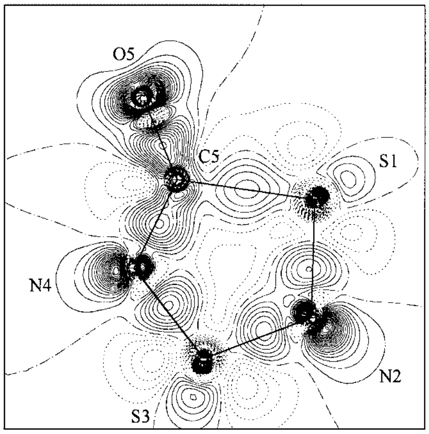

Figure 6. Deformation electron density of Roesky's ketone (**1**) in the molecular plane; full lines indicate positive electron density, dashed lines negative electron density and dashed-dotted lines zero electron density; isodensity lines were plotted every 0.05 e·Å^{-3}

and the C=O bond can be interpreted as a true double bond (1.94). The C−S bond (0.74), which is longer than expected, has indeed the lowest electron density between the two nuclei involved in the bond.

As the second part of this qualitative description, an energetic criterion was used as a measure of the (anti/non)aromatic character. For 1,3$\lambda^2\delta^4$,2,4-benzodithiadiazine the UV/Vis absorption spectrum shows a maximum at 617 nm which is due to the heterocycle.[20] Our own measurements performed on Roesky's ketone produce a maximum absorption wavelength of 369 nm. The calculated value of the HOMO−LUMO gap, which is 342 nm at the B3LYP/6-311+G* level, is relatively close to the experimental one. It is known that the HOMO−LUMO separation may serve as an indicator of structural stability and reactivity; in the case of aromaticity, a larger HOMO−LUMO gap indicates a larger aromatic stabilisation (see ref.[19] and references cited therein). Based on this, the difference between the two $\lambda_{\max}$ values of the two compounds can serve to distinguish 5-oxo-1,3,2,4-dithiadiazine (aromatic) from 1,3$\lambda^2\delta^4$,2,4-benzodithiadiazine (antiaromatic). The three criteria form a consistent set. As already mentioned in the introduction, the properties of compounds containing an NSNS fragment differ considerably from those of their hydrocarbon analogues. This can be illustrated here again by comparing Roesky's ketone (6 π-electrons), which is clearly aromatic, with its hydrocarbon analogue, the antiaromatic cyclopentadienone (4 π-electrons). These findings are in agreement with Hückel's $4n + 2$ π-electron rule.[21] In 1972 Banister[22] proposed that planar sulfur−nitrogen heterocycles are electron-rich compounds that show aromaticity, in agreement with Hückel's rule. He supported this contention with S_2N_2, S_4N_3 and S_5N_5 as examples. In our study we see that the aromaticity of our ring system, containing a carbonyl group besides the nitrogen and sulfur atoms, complies with Hückel's rule as well.

After this successful qualitative description of the aromaticity of the title compound, an attempt was made to obtain a quantitative insight into the combination of calculated bond orders, bond lengths and NICS values so that a description of the degree of aromaticity could be constructed. To do this, three constitutional isomers of 5-oxo-1,3,2,4-dithiadiazole (**1**), in which the sulfur and nitrogen atoms are permutated, were included in the calculations. The structures of the isomers 5-oxo-1,2,3,4-dithiadiazole (**2**), 5-oxo-1,4,2,3-dithiadiazole (**3**) and 5-oxo-2,3,1,4-dithiadiazole (**4**) are given in Figure 1. The molecular geometries, bond orders, total energies and NICS values of these three compounds are given in Table 5; the data for Roesky's ketone (**1**) is added for comparison. The NICS(0) values, calculated in the molecular plane, are negative for all isomers. It has been pointed out by Schleyer et al.[23] that there are some artifacts in NICS(0) values calculated in the plane of the molecule, due to the σ-framework of the molecule. In order to circumvent this, they proposed to calculate NICS(1) values at 1 Å above the ring center, since aromaticity rather involves the delocalization of the π-electrons. Based on the NICS(0) values, all molecules are aromatic. For **3** the NICS(0) and NICS(1) values are almost equal and considerably smaller than for the other isomers, suggesting that this isomer is nonaromatic. The bond orders and bond lengths of **3** indicate that all bonds are single, except the N=N and C=O bonds, which are localized double bonds. The localized nature of the latter bond is found in all isomers and we conclude that these π-electrons do not play any role in stabilizing the ring. The fact that all other bonds in **3** are single or localized double bonds is in accordance with the magnetic criterion NICS, and together they confirm that 5-oxo-1,4,2,3-dithiadiazole (**3**) is nonaromatic.

The other three isomers — **1**, **2** and **4** — all have larger negative values for NICS(0) and considerably negative values of NICS(1). These compounds must, therefore, all be aromatic, and the most aromatic of the series, according to this magnetic criterion, is 5-oxo-2,3,1,4-dithiadiazole (**4**). For this compound all bond orders have a value of about 1.00, which suggests there is maximum electron delocalization, i.e. a very narrow range of bond-order values of the bonds in the five-membered ring. This is in agreement with the two NICS values. The two remaining compounds, 5-oxo-1,3,2,4-dithiadiazole (**1**) and 5-oxo-1,2,3,4-dithiadiazole (**2**), could be classified as being of intermediate aromaticity, even though the structural and magnetic criteria put them in a different order.

We notice here that the overestimation of the C−S bond length at the B3LYP/6-311+G* level of theory has apparently no influence on the description of the electron delocalisation, whereas the excellent description of the relative bond lengths in the NSNS fragment by this method is obviously very important.

As a more general conclusion it can be stated that it is possible to qualitatively determine the (anti/non)aromatic nature of a system by combining structural, energetic and magnetic criteria. Some general quantitative trends can be found as well, even though a real numerical determination of the degree of aromaticity for Roesky's ketone (**1**) and its three studied isomers does not lead to an unambiguous order of aromaticity. Since these isomers cannot be interrelated by isodesmic reactions, no conclusion pertaining to their aromaticity can be drawn from the total energy values, which are also given in Table 5. The energy differences contain both different contributions due to the different kinds of bonds in the isomers and contributions due to the aromatic stabilization. Because these contributions cannot be separated, the total energies cannot be used as an aromaticity criterion.

Reactivity and Reactive Sites

We finally turn our attention to the local reactivity description by means of the condensed Fukui functions and local softnesses calculated for Roesky's ketone (**1**); these are given in Table 6. The stockholder charges, discussed above, will be used in this reactivity description as well. For all details on Fukui functions and local softnesses, and on the related global and local softness and hardness concept, we refer the reader to a recent review.[24] We mention here that a maximum value of the Fukui function, f^+, and local softness, s^+ (or f^- and s^-), indicates the most suitable place for nucleophilic (or electrophilic) attack by a soft species. As can be seen from Table 6, S3 has the largest s^+ value, and it also has the largest positive charge (Table 3). From these findings we know that S3 is the preferred site for a nucleophilic attack both by soft and hard reagents. The most likely site for an electrophilic attack is S1, but in view of its positive charge one does not expect a charge-controlled electrophilic attack to take place at this atom; rather, S1 is the favoured site for an orbital-controlled (based on the Fukui functions) electrophilic attack. The question of which site in Roesky's ketone (**1**) *is* favoured for a charge-controlled electrophilic attack can be answered in the following way.

The next highest value of f^- in Table 6 is found for S3 but, again, this site is disfavoured for a charge-controlled electrophilic attack due to its high positive atomic charge. Just below the value of S3 we find O5 and, even though it has a lower local softness value for electrophilic attack than both sulfur atoms, it has a pronounced negative charge and therefore is the most likely site for the charge-controlled attack by a hard electrophile. This has indeed been observed experimentally:[11] reactions between Roesky's ketone and electron-deficient hard Lewis acids like BF_3, $SbCl_5$ and $SnCl_4$ always yield adducts in which the metal atom is coordinated to the oxygen atom, the site predicted by assuming a charge-controlled regioselectivity.

Finally, we note that the local softness can also be seen as a measure of the ability of an atom to adapt its charge when electrons are added to or removed from a molecule. Upon inspection of the calculated stockholder charges of the cationic and anionic forms of Roesky's ketone (Table 3), we indeed find that the sulfur atoms — the softest atoms — are most suited as electron donor and as electron acceptor: upon oxidation or reduction of **1** the change of the atomic charge of both sulfur atoms is the largest in the molecule. More qualitatively, the softness of an atom can also be expressed by the diffuseness of the electron cloud surrounding it, and in this context we refer to the figure containing the deformation electron-density map (Figure 6): the lone pairs on the sulfur atoms — the softest atoms — are more diffuse than the ones on the harder nitrogen atoms.

Table 6. Fukui functions, f^+ and f^-, and local softnesses, s^+ and s^-, of the different atoms in Roesky's ketone (**1**)

	f^+	s^+	f^-	s^-
S(1)	0.256	0.864	0.280	0.945
N(2)	0.151	0.509	0.107	0.360
S(3)	0.320	1.082	0.212	0.715
N(4)	0.108	0.364	0.137	0.461
C(5)	0.056	0.191	0.064	0.216
O(5)	0.110	0.370	0.202	0.682

Conclusions

5-Oxo-1,3,2,4-dithiadiazole was synthesized and its structure re-determined experimentally by single-crystal X-ray diffraction. The experimental molecular geometry was compared to the B3LYP/6-311+G* geometry and a good agreement was found, except for the C−S bond, which is overestimated by the calculation. Further molecular and atomic properties were calculated at this level to obtain insight into the structure, aromaticity and reactivity of the title compound. A Hirshfeld partitioning of the electron density was used to calculate the atomic charges and dipoles, which led directly to the understanding of the origin of the molecular dipole. Based on frontier-orbital topologies, the geometries of the ionic forms of Roesky's ketone were explained. A consistent combination of structural, magnetic and energetic criteria confirmed that the compound is aromatic. An attempt to quantify the aromaticity, based on NICS values, bond lengths, bond orders and deformation densities, was made, and even though some general trends can be found, a real quantification was not possible for these compounds. Finally, a number of reactivity descriptors from conceptual DFT were calculated and the reactive sites within the molecule could be identified.

We note that, based on the finding that the π-system in the heterocycle of Roesky's ketone is delocalised over the entire ring, it would be incorrect to use the λ,δ-nomenclature, as this suggests localisation. The contrast between 1,3$\lambda^2\delta^4$,2,4-benzodithiadiazine (localised π-system and antiaromatic compound) and 5-oxo-1,3,2,4-dithiadiazole (**1**; delocalised π-system and aromatic compound) can now be conveniently made by omitting the λ,δ descriptors.

Experimental Section

Synthesis: 5-Oxo-1,3,2,4-dithiadiazole (**1**) was synthesised by a modification of a procedure reported by Neidlein and Gieren;[9] the reaction sequence is given in Figure 2. Unless otherwise stated, manipulations were performed under oxygen-free argon using standard Schlenk techniques and flame-dried Schlenk glassware. Hexane and chloroform were dried, purified and stored according to common procedures.[25] Chlorocarbonylsulfenyl chloride was purchased from Lancaster and used as received; bis(trimethylsilyl)sulfur diimide was prepared according to a literature method.[26] The UV/Vis absorption spectrum was obtained from a solution in dry CH_2Cl_2 with a Hitachi U-2001 double-beam spectrometer. A solution of bis(trimethylsilyl)sulfur diimide (5.23 g, 5.97 mL, 25.33 mmol) in chloroform (30 mL) was added dropwise over a 40 min period to a stirred and cooled (0 °C) solution of chlorocarbonylsulfenyl chloride (3.32 g, 2.10 mL, 25.35 mmol) in chloroform (30 mL). Once the addition was complete, the stirred reaction mixture was slowly warmed to room temperature, then heated to 40 °C for 20 min and then allowed to cool to room temperature. Hexane (60 mL) was added and the mixture was filtered through a stainless steel cannula to remove any insoluble material. The volume of the filtrate was reduced in vacuo to approximately 50 mL and then stored at −14 °C overnight. The resulting yellow crystalline material was collected by suction filtration, washed with cooled (0 °C) hexane (10 mL) and then dried briefly in vacuo. The yield was 1.63 g (53%). UV/Vis (CH_2Cl_2): $\lambda_{max} = 369$ nm.

X-ray Structure Determination: Single crystals of 5-oxo-1,3,2,4-dithiadiazole (**1**) suitable for X-ray diffraction studies were obtained by slow sublimation of the bulk material at room temperature and pressure under argon over a two month period. Crystal structure data for the compound were collected at 125 K with a Bruker SMART CCD diffractometer equipped with an Oxford Instruments low-temperature attachment, using Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Refinements were performed using SHELXTL (Version 5.10, Bruker AXS, 1999). Crystal data for 5-oxo-1,3,2,4-dithiadiazole (**1**): CN_2OS_2, M = 120.15, orthorhombic, a = 13.029(3), b = 12.762(3), c = 9.145(2) Å, V = 1520.6(6) Å^3, T = 125(2) K, space group $Pbca$, Z = 16 with two nonequivalent molecules in the asymmetric unit, D_c = 2.099 g·cm^{-3}, μ(Mo-K_α) = 1.207 mm^{-1}, 1359 unique reflections (R_{int} = 0.0206) measured. Final R_1 [1097, $F \geq 2\sigma(F)$] = 0.0225, wR (all F^2) = 0.0580. CCDC-238171 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Calculations: All calculations were performed on isolated molecules using the BRABO[27] and Gaussian 98[28] suites of programs applying the Density Functional level of theory (DFT), using the Becke-type three-parameter hybrid functional,[29] B3LYP[30] and the 6-311+G*[31,32] basis set. Initially, the geometry of Roesky's ketone was calculated in C_1 symmetry, but the structure converted into a planar conformation. Consequently, the symmetry was raised to C_s, the geometry was re-calculated and a frequency calculation was performed to ascertain that the resulting structure was indeed an energy minimum. All subsequent calculations of molecular properties were performed at the B3LYP/6-311+G* geometry. Deformation densities were calculated by subtracting the pro-molecular density from the total molecular density. Stockholder charges were calculated as previously reported,[15] based on the Hirshfeld partitioning of the space.[33] Atomic dipole moments, μ_A, were calculated according to

$$\mu_{A,n} = -\int r_n \Delta\varrho_A(\vec{r})\,d\vec{r}$$

with $n = x, y, z$, $\vec{r}$ = the position vector of the atom and $\Delta\rho$ = the deformation density, as usually defined.[16] Nucleus-Independent Chemical Shifts (NICS)[34] were calculated at the B3LYP/6-311+G* level of theory, in the geometrical centre of the ring [NICS(0)] and at a distance of 1 Å perpendicularly above the ring centre [NICS(1)], using the Gauge Independent Atomic Orbitals (GIAO) method as implemented in Gaussian 98. Bond orders were calculated according to Mayer's definition.[35] The Fukui function[36] was calculated by the finite difference approach.[24] Geometries and molecular properties of the three constitutional isomers **2**−**4** and the anionic and cationic forms of Roesky's ketone (**1**) were calculated at the B3LYP/6-311+G* level. A procedure analogous to the one applied to the parent compound indicated that the constitutional isomers and the ionic forms also have C_s symmetry. Cartesian coordinates and energies of all compounds are given in the Supporting Information.

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