chen Entladungen in NH_3 erscheinen, in N_2H_4-Entladungen im abgeschlossenen System erst nach einiger Zeit vorkommen und nach längerer Entladungsdauer wieder verschwinden. Die Intensitäten der Emissionen I, II und III nehmen zu, wenn die Intensität der Schuster-Bande zunimmt und umgekehrt. Da die Schuster-Bande von angeregten Hydrazin-Molekülen emittiert wird, liegt der Verdacht nahe, daß die Emissionen I, II und III auch von einer intermediär auftretenden mehratomigen Species (mehr als 2 Atome) emittiert werden. In Frage kommen: NH_3* (Rotationsschwingungsbanden), N_2H_2*, N_2H_3*, N_2H_4*. Die Emission II könnte evtl. mit der Rotationsschwingungsbande $5\,\nu_1$ von NH_3 bei 6450 Å [9] identisch sein.

Das Verhalten der Intensitäten der H_α-Linie und der Schuster-Bande spricht für Hypothese (1 c) [2]:

Bei kleinen Leistungsdichten im NH_3-Gas ist zwar [H] niedrig, aber N_2H_3- und N_2H_4-Moleküle werden unter diesen schwachen Entladungsbedingungen noch nicht dissoziiert: [N_2H_4*] ist relativ hoch; die H-Atome werden bei der N_2H_4*-Bildung weitgehend aufgebraucht (Abbildung 1 a). Bei höherer Leistungsdichte nimmt [H] schnell zu, jedoch die Zerstörung der N_2H_3- und N_2H_4-Moleküle setzt bereits ein, so daß trotz höherem [H] jetzt [N_2H_4*] abnimmt (Abbildung 1 a, 1b).

In der N_2H_4-Entladung im abgeschlossenen System ist anfangs [N_2H_4*] relativ gering, da offenbar [N_2H_3] noch niedrig ist (Abbildung 3 a). Nach kurzer Zeit ist [N_2H_4*] deutlich angestiegen. Jetzt werden mehr H-Atome zur N_2H_4*-Bildung verbraucht als erzeugt werden: [H] fällt (Abbildung 3 b). Danach überwiegen Dissoziationsreaktionen, wodurch [H] sehr groß wird und [N_2H_4*] stark zurückgeht (Abbildung 3 d).

Zu erwähnen bleibt noch, daß die Schuster-Bande von der stillen Entladung in Hydrazin-Dampf stets emittiert wird, während sie in Glimmentladungen nie beobachtet wurde [10, 11].

[1] A. Schuster, Brit. Assoc. Report **76**, 38 [1872].
[2] R. Weisbeck u. A. Völkner, Chem.-Ing.-Techn. **42**, 31 [1970].
[3] K. Dressler u. D. A. Ramsay, Phil. Trans. Roy. Soc. A **251**, 553 [1959].
[4] R. W. Lunt, J. E. Mills u. E. C. W. Smith, Trans. Faraday Soc. **31**, 792 [1935].
[5] E. J. Willey, Trans. Faraday Soc. **39**, 234 [1943].
[6] R. Weisbeck u. A. Völkner, Z. Angew. Phys. **32**, 258 [1971].
[7] J. C. Devins u. M. Burton, J. Amer. Chem. Soc. **76**, 2618 [1954].
[8] M. Gehring, K. Hoyermann, H. Gg. Wagner u. J. Wolfrum, Ber. Bunsenges. Physik. Chem. **73**, 956 [1969].
[9] R. M. Badger u. R. Mecke, Z. Phys. Chem. B **5**, 333 [1929].
[10] A. Koenig u. O. H. Wagner, Z. Phys. Chem. Abt. A **144**, 219 [1929].
[11] E. F. Logan u. J. M. Marchello, J. Chem. Physics **49**, 3929 [1968].

The Molecular Zeeman Effect in Selenophene

W. Czieslik, D. Sutter, and H. Dreizler

Abteilung Chemische Physik im Institut für Physikal. Chemie Universität Kiel

and C. L. Norris, S. L. Rock, and W. H. Flygare

Noyes Chemical Laboratory, Univtersity of Illinois Urbana, Illinois, USA

(Z. Naturforsch. **27 a**, 1691—1694 [1972]; received 28 September 1972)

The molecular Zeeman effect in the rotational spectrum of selenophene has been observed. The molecular g-values and the magnetic susceptibility anisotropies for selenophene ^{80}Se are: $g_{aa} = -0.0849 \pm 0.0012$, $g_{bb} = -0.0428 \pm 0.0011$, $g_{cc} = +0.365 \pm 0.0010$, $2\,\chi_{aa} - \chi_{bb} - \chi_{cc} = 50.15 \pm 0.80$, $2\,\chi_{bb} - \chi_{cc} - \chi_{aa} = 51.83 \pm 1.3$. From the comparison of the value $\Delta\chi = 2\,\chi_{cc} - \chi_{aa} - \chi_{bb}$ in furan, thiophene and selenophene we conclude that the aromaticities of these molecules would be in the order: furan $<$ thiophene $\cong$ selenophene.

The analysis of the Zeeman effect in the rotational spectrum of selenophene was started almost simultaneously at Kiel and Urbana. Since the experiments were at a rather advanced stage when the two groups became aware of working on the same molecule, it was decided to have a joint publication. The results from both laboratories are in good agreement. This work extends earlier investigations on aromatic five membered rings [1, 2] to fourth row heteroatoms.

Reprint requests to Dr. D. Sutter, Institut für Physikal. Chemie der Universität Kiel, Abteilung Chemische Physik, *D-2300 Kiel*, Olshausenstraße 40—60.

The sample was prepared by passage of dried ethyne through a flask containing a mixture of 10 g selenium and 5 g residue of previous runs at a reaction temperature of 350—400 °C [3 a-c]. This black residue seems to have a catalytic effect because it was essential for a good yield. The reaction product, a brown oil, was purified by distillation under normal pressure. The best fraction had a percentage purity of 95% selenophene as was checked by gas chromatography. The yield was 20% ($Se_{selenophene}/Se_{input} = 0.2$).

The Zeeman microwave spectrographs used in this work have been described before [4, 5]. The microwave spectra of selenophene have been assigned previously [6] and the transitions were found with no difficulty. Tables 1 and 2 show the observed and calculated splittings. (Urbana measurements are marked with an asterisk. The ^{78}Se-species was measured at Kiel University only.) The analysis of the Zeeman splittings followed the same procedure as was described in Ref. [2]. (For a derivation of the Hamiltonian which starts from the Lagrange function see Ref. [7, 8]. The perturbation treatment including higher order terms in the magnetic field strength is given in Appendix AI of Ref. [5].) Table 3 shows the diagonal elements of the g-matrix

Table 1. Zeeman-spectra of selenophene Se-80 species (Urbana measurements are marked with an asterisk).

Transition Frequency (MHz) H (KGauss)	$M_l - M_u$		int.	$\Delta\nu_{exp}$ (kHz)	$\Delta\nu_{cal}$ (kHz)	Diff. (kHz)
111–212						
10403.660						
$H = 24.14$	1–	1	3	−1115.0	−1111.9	− 3.1
111–212						
10403.630						
$H = 22.03$	1–	2	12	− 129.0	− 126.5	− 2.5
	−1–	−2	12	884.0	892.9	− 8.9
111–212						
10403.660						
$H = 22.26$	1–	2	12	− 125.0	− 123.7	− 1.3
	0–	1	6	80.0	75.2	4.8
	−1–	−2	12	915.0	906.5	8.5
101–202						
11276.175						
$H = 24.14$	1–	1	3	− 531.0	− 547.4	16.4
	−1–	−1	3	− 418.0	− 406.4	−11.6
	0–	0	4	22.0	30.4	− 8.4
101–202						
11276.175						
$H = 24.37$	1–	2	12	136.0	137.1	− 1.1
110–211						
12490.372						
$H = 24.15$	1–	1	3	211.0	179.5	31.5
	−1–	−1	3	1202.0	1182.9	19.1
110–211						
12490.372						
$H = 21.65$	0–	−1	6	−1256.0	−1264.7	8.7
	1–	2	12	296.0	267.5	28.5
212–313						
15506.168						
$H = 24.14$	2–	2	5	−1018.0	−1004.3	−13.7
212–313						
15506.168						
$H = 22.04$	0–	−1	12	272.0	293.8	−22.8
202–303						
16515.371						
$H = 22.03$	−2–	−3	30	477.0	479.1	− 2.1
221–322						
17170.544						
$H = 24.14$	0–	0	9	− 348.0	− 351.5	3.5
	−1–	−1	8	308.0	325.7	−17.7
	−2–	−2	5	1358.0	1354.5	3.5
221–322						
17170.544						
$H = 22.27$	0–	1	12	225.0	217.9	7.1
220–321						
17825.672						
$H = 24.14$	0–	0	9	− 233.0	− 220.5	−12.5
	−1–	−1	8	339.0	356.3	−17.3
220–321						
17825.672						
$H = 22.27$	−1–	−2	20	− 473.0	− 491.5	18.5
211–312						
18618.543						
$H = 24.14$	−2–	−2	5	655.0	663.4	− 8.4
211–312						
18618.543						
$H = 21.45$	−2–	−3	30	− 148.0	− 130.0	−18.0
211–312						
18618.543						
$H = 24.38$	−2–	−3	30	− 134.0	− 137.0	3.0
322–423						
22760.223						
$H = 24.16$	1–	1	15	− 330.0	− 346.5	16.5
	0–	0	16	− 152.0	− 151.8	− 0.2
	−1–	−1	15	105.0	88.4	16.6
	−2–	−2	12	374.0	374.2	− 0.2
	−3–	−3	7	707.0	705.5	1.5
101–202						
11276.174						
$H = 21.14$	1–	1	3	− 421.0	− 427.4	6.4*
	−1–	−1	3	− 298.0	− 304.0	6.0*
	0–	0	4	17.0	23.3	− 6.3*
111–212						
10403.660						
$H = 21.12$	0–	0	4	− 158.0	− 158.2	0.2*
	−1–	−1	3	− 21.0	− 28.6	7.6*
110–211						
12490.372						
$H = 21.14$	0–	0	4	− 480.0	− 488.6	8.6*
	1–	1	3	81.0	82.9	− 1.9*
221–322						
17170.544						
$H = 21.14$	1–	1	8	− 579.0	− 573.9	− 5.1*
	0–	0	9	− 255.0	− 269.6	14.6*
	−1–	−1	8	310.0	304.4	5.6*
212–313						
15506.168						
$H = 21.13$	1–	1	8	− 297.0	− 300.3	3.3*
	−2–	−2	5	− 297.0	− 292.5	− 4.5*
	0–	0	9	− 34.0	− 48.6	14.6*
	−1–	−1	8	− 34.0	− 46.0	12.0*
211–312						
18618.543						
$H = 21.12$	1–	1	8	− 123.0	− 144.6	21.6*
	0–	0	9	− 123.0	− 109.5	−13.5*
	−1–	−1	8	106.0	118.9	−12.9*
101–202						
11276.174						
$H = 17.28$	1–	2	12	43.0	51.8	− 8.8*
	0–	1	6	128.0	125.6	2.4*
	0–	−1	6	155.0	142.1	12.9*
	−1–	−2	12	155.0	169.2	−14.2*
111–212						
10403.660						
$H = 21.11$	1–	2	12	− 158.0	− 136.5	−21.5*
	0–	1	6	60.0	65.1	− 5.1*
	0–	−1	6	136.0	164.8	−28.8*
	−1–	−2	12	841.0	840.5	0.5*
111–212						
10403.660						
$H = 17.22$	1–	2	12	− 164.0	− 164.2	0.2*
110–211						
12490.372						
$H = 17.27$	−1–	−2	12	− 44.0	− 54.9	10.9*
	0–	1	6	64.0	65.2	− 1.2*
	1–	2	12	187.0	195.6	− 8.6*
202–303						
16515.371						
$H = 21.15$	2–	3	30	− 65.0	− 68.4	3.4*
	1–	2	20	10.0	0.4	9.6*
	−1–	−2	20	363.0	354.0	9.0*
	−2–	−3	30	448.0	452.0	− 4.0*
212–313						
15506.168						
$H = 21.10$	2–	3	30	− 233.0	− 233.9	0.9*
	1–	2	20	− 60.0	− 31.1	−28.9*
	−1–	−2	20	587.0	576.7	10.3*

Table 2. Zeeman-spectra of selenophene Se-78 species.

Transition Frequency (MHz) H (KGauss)	$M_l - M_u$		int.	$\Delta\nu_{exp}$ (kHz)	$\Delta\nu_{cal}$ (kHz)	Diff. (kHz)
111–212						
10472.972						
$H = 22.26$	1–	2	12	– 136.0	– 138.3	2.3
	0–	1	6	81.0	77.5	3.5
	–1–	–2	12	897.0	910.3	–13.3
101–202						
11354.751						
$H = 24.15$	1–	1	3	– 539.0	– 538.5	– 0.5
	–1–	–1	3	– 400.0	– 395.7	– 4.3
	0–	0	4	18.0	22.8	– 4.8
101–202						
11354.751						
$H = 24.38$	1–	2	12	131.0	123.7	7.7
110–211						
12589.531						
$H = 24.15$	0–	0	4	– 635.0	– 628.3	– 6.7
	1–	1	3	187.0	189.0	– 2.0
	–1–	–1	3	1188.0	1188.2	– 0.2
110–211						
1289.531						
$H = 22.26$	1–	2	12	244.0	258.0	–14.0
212–313						
15606.978						
$H = 22.27$	2–	3	30	– 254.0	– 246.9	– 7.1
202–303						
16621.098						
$H = 22.27$	2–	3	30	– 91.0	– 72.6	–17.4
	0–	–1	12	137.0	136.7	0.3
221–322						
17296.864						
$H = 24.16$	0–	0	9	– 351.0	– 342.1	– 8.9
	–1–	–1	8	312.0	328.8	–16.8
211–312						
18763.131						
$H = 24.38$	–2–	–3	30	– 136.0	– 126.0	–10.0
322–423						
22924.196						
$H = 24.16$	–1–	–1	15	96.0	90.2	5.8
	–2–	–2	12	375.0	374.1	0.9
	–3–	–3	7	714.0	702.6	11.4

and the anisotropies of the magnetic susceptibilities. In order to give an idea of the experimental uncertainties the Kiel and Urbana results are listed separately. Note that from theoretical reasons the susceptibilities should be the same for the two isotopic species. In further calculations an average of the g-values and susceptibility anisotropies in Table 3 are used.

The molecular quadrupole moments can be obtained directly from the Zeeman parameters in Table 3 and the rotational constants [see Eq. (3) of Ref. [2]], and the results are listed in Table 4. Since in the case of selenophene the geometry of the nuclear frame is known from a very extensive r_s structure determination [6], it is possible to use the magnetic constants given in Table 3

Table 3. Zeeman parameters of selenophene. The susceptibility anisotropies are given in units of 10^{-6} erg/(G² mole). The experimental uncertainties given in the table are twice the standard deviations.

	^{80}Se-species (Kiel)	^{80}Se-species (Urbana)	^{78}Se-species
g_{aa}	– 0.0844	– 0.0854	– 0.0840
	± 0.0014	± 0.0010	± 0.0016
g_{bb}	– 0.0432	– 0.0423	– 0.0432
	± 0.0012	± 0.0010	± 0.0014
g_{cc}	0.0365	0.0365	0.0372
	± 0.0010	± 0.0010	± 0.0010
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	50.56	49.74	49.11
	± 1.0	± 1.2	± 1.0
$2\chi_{bb} - \chi_{cc} - \chi_{aa}$	53.10	50.56	53.80
	± 1.6	± 2.0	± 1.7

Table 4. Molecular constants of selenophene ^{80}Se. The molecular quadrupole moments are in units of 10^{-26} esu cm², the susceptibilities in units of 10^{-6} erg/(G² mole), and the sums of the squares of the nuclear or electronic coordinates in units of 10^{-16} cm². For the bulk susceptibility taken from Ref. [9] a 10% uncertainty was assumed since no experimental value was available to us. The calculation is based on the average values of Table 3 (^{80}Se-species only) namely $g_{aa} = -0.0849$, $g_{bb} = -0.0428$, $g_{cc} = +0.0365$, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 50.15$, $2\chi_{bb} - \chi_{cc} - \chi_{aa} = 51.83$.

Q_{aa}	2.1 ± 1.7
Q_{bb}	6.5 ± 2.2
Q_{cc}	– 8.6 ± 2.8
χ^p_{aa}	194.7 ± 1.2
χ^p_{bb}	359.0 ± 2.4
χ^p_{cc}	469.7 ± 2.6
$\langle \lvert \sum (a_i^2 - b_i^2) \rvert \rangle$	38.6 ± 1.0
$\langle \lvert \sum (b_i^2 - c_i^2) \rvert \rangle$	38.2 ± 0.8
$\langle \lvert \sum (c_i^2 - a_i^2) \rvert \rangle$	– 76.8 ± 0.9
$\sum Z_n a_n^2$	78.2 ± 0.4
$\sum Z_n b_n^2$	40.3 ± 0.2
$\sum Z_n c_n^2$	0.0 ± 0.0
$(\chi_{aa} + \chi_{bb} + \chi_{cc})/3$	66.8 ± 6.7
χ_{aa}	– 50.1 ± 7.0
χ_{bb}	– 49.5 ± 7.1
χ_{cc}	– 100.8 ± 7.4
$\langle \lvert \sum a_i^2 \rvert \rangle$	86.5 ± 3.4
$\langle \lvert \sum b_i^2 \rvert \rangle$	47.9 ± 3.4
$\langle \lvert \sum c_i^2 \rvert \rangle$	9.8 ± 3.4
χ^d_{aa}	– 244.8 ± 8.2
χ^d_{bb}	– 408.5 ± 9.5
χ^d_{cc}	– 570.5 ± 10.0

to compute the individual components of the paramagnetic susceptibility [Eq. (8) in Ref. [2]], and the anisotropies of the second moments of the electronic charge distribution [Eq. (10) in Ref. [2]]. The results are given in Table 4 together with the sums running over the nuclei $\sum_n Z_n a_n^2$, $\sum_n Z_n b_n^2$ and $\sum_n Z_n c_n^2$ (Z_n = atomic number; a_n, b_n, $c_n = a$, b, and c coordinate of the n-th nucleus respectively). The uncertainties for these sums have been calculated from the rotational constants given in Ref. [6] when different sets of isotopic species were used for the r_s structure determination.

If one includes the bulk magnetic susceptibility, $\chi = (\chi_{aa} + \chi_{bb} + \chi_{cc})/3$, which, however, has been measured in the liquid phase only [9], one can obtain the individual elements of the susceptibility tensor. This in turn makes it possible to compute the second momets of the electronic charge distribution individually [Eq. (15) in Ref. [2]]. They are given in the lower part of Table 4 together with the elements of the diamagnetic susceptibility tensor.

It is interesting to compare the out-of-plane minus the average in-plane magnetic susceptibility anisotropy obtained here $[\Delta\chi = \chi_{cc} - \frac{1}{2}(\chi_{aa} + \chi_{cc}) = -51.0]$ with the corresponding values in furan (-38.7) and thiophene (-50.1). Apparently the anisotropy, which is related to the ring current, increases in thiophene (relative to furan) but no further increase is observed in selenophene. The magnetic susceptibility anisotropies in the OCO, OCS, and OCSe series [10] indicate that the local atomic anisotropies of S and Se will not be greatly different and only slightly larger than O [11]. Thus, we would conclude that the ring currents and the corresponding aromaticities of the furan, thiophene, and selenophene series would be in the order

$$\text{furan} < \text{thiophene} \cong \text{selenophene}.$$

If one considers the ionization potential of the heteroatom (see Ref. [9], Table E 74) as indicative of electron localization, one obtains the same order as above for electron delocalization. However quite different conclusions are obtained from magnetic susceptibility anisotropies measured by an *indirect* method based on the differences in the chemical shifts between α- and β-ring protons in the three rings [12].

Since our measurement of anisotropies is a direct one, we feel that our conclusion as to the relative aromaticities of these rings: furan $<$ thiophene $\cong$ selenophene, is the correct one.

Acknowledgement

The support of the Deutsche Forschungsgemeinschaft, Fonds der Chemie, and the U.S. National Science Foundation are gratefully acknowledged.

[1] D. SUTTER and W. H. FLYGARE, J. Amer. Chem. Soc. **91**, 6895 [1969].
[2] D. SUTTER and W. H. FLYGARE, J. Amer. Chem. Soc. **91**, 4063 [1969].
[3] a) L. CHIERICI and G. PAPPALARDO, Gazz. Chim. Ital. **88**, 453 [1958]; b) H. V. A. BRISCOE and J. P. PEEL, J. Chem. Soc. **1928**, 1741; c) H. V. A. BRISCOE, J. B. PEEL, and P. L. ROBINSON, J. Chem. Soc. **1928**, 2628.
[4] W. H. FLYGARE, W. HÜTTNER, R. L. SHOEMAKER, and P. D. FOSTER, J. Chem. Phys. **50**, 1714 [1969].
[5] D. SUTTER, Z. Naturforsch. **26 a**, 1644 [1971].
[6] N. M. POZDEEV, O. B. AKULININ, A. A. SHAPKIN, and N. N. MAGDESIEVA, Zh. Strukt. Khim. **1970**, 869. — R. D. BROWN, F. R. BURDEN, and P. D. GODFREY, J. Mol. Spect. **25**, 415 [1968].
[7] D. SUTTER, A. GUARNIERI, and H. DREIZLER, Z. Naturforsch. **25 a**, 222, 2005 [1970].
[8] B. HOWARD and R. E. MOSS, Mol. Phys. **19**, 433 [1970]; Z. Naturforsch. **25 a**, 2004 [1970].
[9] Handbook of Chemistry and Physics 51st. Edition (1970–1971), E 137, The Chemical Rubber, Cleveland/Ohio.
[10] R. L. SHOEMAKER and W. H. FLYGARE, Chem. Phys. Letters **6**, 576 [1970].
[11] For further discussion of the similarity of the local group anisotropies for O and S atoms see R. C. BENSON, Ph. D. Thesis, University of Illinois, Urbana, Illinois.
[12] N. N. MAGDESIEVA, Adv. in Heterocyclic Chem. **12**, 1 [1970].

Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Konrad Triltsch, Würzburg