stirred at room temperature until it became yellowish-green. The product was recrystallized from 10 ml of ether. Yield 70–75 % based on the amount of the selenenyl bromide.

[Ph_4As^+][p-$XPhSeSO_3^-$]. The aromatic seleno Bunte salts were prepared from the corresponding selenenyl benzenesulfinates, $Na_2SO_3.7H_2O$, and $Ph_4AsCl.2H_2O$ according to the following procedure. A solution, made by dissolving 3.4×10^{-3} mol of the aromatic selenenyl sulfinate in 15 ml of ether, was added under vigorous stirring at room temperature to a solution containing 3.8×10^{-3} mol of each of the reagents $Na_2SO_3.7H_2O$ and $Ph_4AsCl.2H_2O$ in 25 ml of water. The reaction mixture was stirred for 5 min, and the product separated as a white crystalline compound. The salt was filtered off, washed carefully with cold water and drained well. The product was recrystallized from about 10 ml of warm acetonitrile by the addition of some ether. Yield *ca.* 85 % based on the amount of selenenyl sulfinate.

[Ph_4As^+][p-$XPhSeSSO_3^-$]. The tetraphenylarsonium salts of aromatic selenenyl thiosulfates were prepared from the corresponding selenenyl benzenesulfinates, $Na_2S_2O_3.5H_2O$, and $Ph_4AsCl.2H_2O$. The procedure is analogous to that described above for the preparation of the corresponding selenenyl sulfite salts. The products, which appeared as yellowish-green compounds, were recrystallized from acetonitrile by the addition of some ether. Yield 85–90 % based on the amount of the selenenyl benzenesulfinate.

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On Comparisons of Structural Information Obtained from Microwave Spectroscopy and from Electron-diffraction Studies of Gaseous Chlorobutatriene and Chlorobutenynes

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In recent electron-diffraction studies on the molecular structures of gaseous C_4H_3Cl isomers[1–4] the moments of inertia calculated from the structural results were compared to values obtained from microwave spectroscopy.[5–9] The comparisons were based upon the assumption that the average distances r_α and r_z[10] are comparable quantities, and the corresponding moments of inertia are given in Table 1. They were derived from the operational parameters, respectively, for electron diffraction (r_a) and microwave spectroscopy (r_o)[10] using similar force fields for computation of the necessary correction terms as described previously.[1–9]

However, r_α should be corrected to r_α^0 in order to represent the distance between the mean positions of a pair of atoms in the zero-point level as does the r_z parameter.[10]

$$r_\alpha^0 = r_\alpha + (K - K_0) - \tfrac{3}{2}a(l^2 - l_0^2) \qquad (1)$$

where K_0 and l_0 are the perpendicular amplitude correction coefficient and the root-mean-square amplitude of vibration at absolute zero, and a is an anharmonicity constant which for bond distances is usually about 2 Å^{-1}.[10] The correction is dominated by the $K - K_0$ term and r_α is therefore smaller than r_α^0 by an amount which was assumed to be negligible. A closer examination of the moments of inertia for all five isomers (Table 1) reveals, however, that those obtained from the electron-diffraction data (r_α) are all smaller than the corresponding microwave ones (r_z). Although the discrepancies are smaller than the estimated error limits,[1–4] the similar trend indicates the presence of some systematic error. The approximation applied by using r_α rather than r_α^0 was therefore reconsidered. The K_0- and l_0-values were computed from the force fields described previously for the five compounds[1–4] and the corresponding moments of inertia based upon r_α^0-parameters ($a = 2$ Å^{-1}) are given in Table 1. The correction introduced removed

Table 1. Comparison of moments of inertia (in au Å²) for chlorobutatriene and chlorobutenynes obtained from microwave spectroscopy (MW) and electron-diffraction (ED) studies.

		r_s(MW) [5–9]	r_α(ED) [1–4]	r_α^0(ED) [b]
Chlorobutatriene [1,5]	I_a	–	20.5 (20.1) [a]	20.6 (20.2) [a]
ClHC=C=C=CH₂	I_b	326.01	322.9 (325.8)	324.5 (327.4)
	I_c	346.20	343.4 (345.8)	345.2 (347.6)
cis-1-Chlorobutenyne [2,6]	I_a	56.60	56.2	56.4
ClHC=CH–C≡CH	I_b	196.86	196.6	197.2
	I_c	253.40	252.8	253.6
trans-1-Chlorobutenyne [2,7]	I_a	–	11.1	11.1
ClHC=CH–C≡CH	I_b	334.88	333.5	334.8
	I_c	345.33	344.6	345.9
2-Chlorobutenyne [3,8]	I_a	73.63	73.5	73.7
H_2C=CCl–C≡CH	I_b	163.41	163.2	163.6
	I_c	237.05	236.7	237.3
4-Chlorobutenyne [4,9]	I_a	–	11.5 (11.5) [a]	11.6 (11.6) [a]
H_2C=CH–C≡CCl	I_b	358.49	356.2 (357.3)	358.7 (359.8)
	I_c	370.60	367.7 (368.8)	370.3 (371.4)

[a] The values for models III and I are given for chlorobutatriene [1] and 4-chlorobutenyne,[4] respectively, while parenthesized values represent models IV and II. [b] The valence angles are assumed to be equl to those of the r_α-models.

the systematic discrepancy between values obtained from the two methods, as seen from Table 1, and a better overall agreement was obtained. The comparisons of the moments of inertia still rest upon approximations as assumed force fields were applied in the computation of the various correction terms. In particular these are sensitive to changes in the force constants associated with the lower fundamental frequencies which are not well known. The uncertainty of the anharmonicity constant is probably of less importance due to the smaller magnitude of the second term compared to the first one in eqn. 1.

It should be noted that the approximation had different impact on the moments of inertia for the five compounds being largest for chlorobutatriene and 4-chlorobutenyne. This is an unfortunate circumstance since for these two molecules the microwave data were used to add credibility to models which represented the best fit to the electron diffraction data but which contained, as it was pointed out, unreasonable values for the C=C–H valence angles (Models IV and II, respectively).[1,4] The results presented in this paper make it necessary to correct the support given to these models as comparisons of moments of inertia now favour models with the C=C–H angles fixed at reasonable values, *i.e.* models III and I, respectively, for chlorobutatriene and 4-chlorobutenyne (see Table 1). In the case of 4-chlorobutenyne information about the Cl···H nonbond distances is also available from the microwave investigation.[9] The Cl···H (etylynic) distances obtained from micrawave data (r_s-values [10]) and electron-diffraction data (r_a-values [10]) compare favourably for *cis*- and *trans*-1-chlorobutenyne.[2,6,7] For 4-chlorobutenyne the r_s-values are 5.024, 6.197, and 4.830 Å, respectively, for the Cl···H_1(*cis*), Cl···H_1(*trans*) and Cl···H_2 distances [9] as compared to the r_a-values of Models I and II, respectively: I, 5.046(10), 6.169(9) and 4.762(8) Å; II, 5.142(47), 6.182(41) and 4.861(36) Å.[4] Comparisons seem to support a combination of models I and II with ∠C=C–H_1 = 122° (I) and ∠C=C–H_2 = 114.6(2.6)° (II). The smaller C=C–H_2 angle of Model II is also favoured by the determination of the amplitude of vibration associated with the Cl···H_2 distance as described previously.[4] The moments of inertia (r_α^0) for the combined model (Model II with ∠C=C–H_1 changed to 122°) are I_a = 11.5, I_b = 359.3 and I_c = 370.7 au Å², and they are in good agreement with the corresponding microwave ones given in Table 1.

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On the Photochemical Behaviour of Radiation Produced Trapped Electrons in an Alcohol/Water Glass

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Radiation produced electrons are stabilized at low temperatures in a variety of solvents among which alcohols and alcohol/water mixtures are the most frequently studied cases. The processes following an ionization event in an alcohol glass are:[1-4]

$$RCH_2OH \xrightarrow{\gamma, X} RCH_2OH^+ + e^- \quad (1)$$

$$e^- \longrightarrow e_t^- \text{ (electron trapping)} \quad (2)$$

$$RCH_2OH^+ + RCH_2OH \longrightarrow RCH_2OH_2^+ + RC{\cdot}HOH \quad (3)$$

(R = H, CH_3, C_2H_5 *etc.*)

The trapped electron, e_t^-, has an absorption spectrum in the visible part of the spectrum and is easily bleached during exposure to visible light, giving rise to alcohol radicals.[5] The nature of this process is somewhat unclear. One possibility is that the photomobilized electrons (e_m^-) react with $RCH_2OH_2^+$ ions [2,5,6] which probably are trapped within a few Ångströms of the electrons, the reactions being:

$$RCH_2OH_2^+ + e_m^- \longrightarrow RCH_2OH + H \quad (4)$$

followed by

$$RCH_2OH + H \longrightarrow RC{\cdot}HOH + H_2 \quad (5)$$

Another possibility would be that mobilized electrons react with neutral alcohol molecules according to the scheme:[7]

$$RCH_2OH + e_m^- \longrightarrow RCH_2O^- + H \quad (6)$$

followed by (5).

To distinguish between the two processes we studied the dependence of the photobleaching efficiency on the dose of ionizing radiation delivered to the sample. We have carried out such an experiment in the case of an ethylene glycol/water glass (1:1 by volume) at 77 K. The results are, as shown below, definitely in favour of the second hypothesis.

We exposed an ethylene glycol/water glass at 77 K to the radiation from a 4 MeV modified AEI-linear accelerator. The samples were prepared by allowing 20 μl drops of sample solution to fall into liquid N_2. The irradiated samples were analyzed by ESR methods. Fig. 1 shows how the yield of trapped electrons and ethylene glycol radicals varies with the dose. It can be seen that while the yield of ethylene glycol radicals increases practically linearly with the dose, the electron yield reaches a plateau.

A similar dose dependence of the electron yield has been reported for a variety of solvents. Thus, the yields are generally reaching a maximum and then decreasing (see review article in Ref. 8). A number of explanations of this behaviour has been proposed: (1) only a limited number of electron traps exist,[9] (2) reactions of the electrons with radicals in the sample [10] and (3) reactions of mobile electrons with positive ions produced by the radiation, or reactions of mobile positive ions with trapped electrons.[11] The maximum concentration of trapped electrons was found to be of the order of 5×10^{-3} M, which is in correspondence with the findings of others for alcohol matrices (see review in Ref. 8).

The samples could be optically bleached by exposing them to the light of a 200 W high pressure mercury lamp fitted to a Bausch & Lomb grating monochromator. Except for the lowest dose (500 krad) the ESR signals from trapped electrons decreased practically linearly with the exposure time during bleaching. This shows that with exception of the first case the samples are total absorbing thus explaining the apparent low quantum efficiency of bleaching at this dose (Fig. 1). For doses exceeding 2 Mrad, Fig. 1 shows that the quantum efficiency of electron bleaching is practically constant. This is true both for bleaching at 366 nm (3.4 eV) and at 625 nm (2.0 eV). The photomobilization threshold for electrons in the present matrix is 2.2 eV.[12] Hence irradiation at 366 nm causes photomobilization of the trapped electrons, while irradiation at 625 nm causes excitation. Since the quantum efficiency of bleaching is dose independent, and since the concentrations of $RCH_2OH_2^+$ as well as