Excited π^* states of divinyl chalcogenides and chalcophenes

V. K. Turchaninov,* L. M. Sinegovskaya, and B. A. Trofimov

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395 2) 46 2952

Electron transitions in divinyl chalcogenides ($CH_2=CHXCH=CH_2$, where X is S, Se, or Te) have been analyzed using UV absorption spectra of dialkyl and alkyl vinyl chalcogenides. The following relations for the orbital energies are found: $\pi \to \sigma^* < \pi \to \sigma^* < \pi \to \pi^* < \pi \to \pi^*$ for Te and $\pi \to \sigma^* < \pi \to \pi^* < \pi \to \pi^* < \pi \to \sigma^*$ for S and Se. For chalcophenes, a correlation between the energy of the excited state (E^*) of specific symmetry, the ionization potential (I) and the electron affinity (EA) is obtained: $E^* = \text{const} + (I + EA)/2$. The electron affinity of divinyl chalcogenides is estimated. The correlation between the excited π^* states of divinyl chalcogenides and chalcophenes is discussed.

Key words: UV and PE spectroscopy; organyl chalcogenides.

Direct information on the relative energy positions of vacant levels (neglecting electron correlation and orbital relaxation) has been obtained so far only for chalcophenes. Two resonances for furan and thiophene arising from ion formation in the $^2B_1$ and $^2A_1$ states have been detected in the range between 0 and 6 eV by transmission spectroscopy (the trapping of low-energy electrons). There is an extra resonance in the transmission spectra of selenophene and tellurophene stemming from the low-lying $^2B_2(\sigma)$ state in ions of these substances. It turned out that the order in which the states with an unpaired electron on the π^*-MO appear is independent of the heteroatom type: $^2B_1 < {}^2A_2$ (see Refs. 1 and 2).

UV-spectroscopy data independently confirm the presence of a low-lying free MO (the π-LUMO) of the b_1 type in chalcophenes. Electron absorption spectra of five-membered heterocycles have been thoroughly analyzed; in particular, it has been established[3–7] that the long-wave $\pi \to \pi^*$ transition in thiophene gives rise to the $^1B_2$ state ($\cdots b^2{}_1 a^1{}_2 b^1{}_1 a^*{}_2$ electron configuration), whereas the short-wave transition results in the $^1A_1$ state ($b^1{}_1 a^2{}_2 b^1{}_1 a^*{}_2$). According to the data on the polarization of $\pi \to \pi^*$ type electron transitions and those on magnetic circular dichroism, chalcophenes can be divided into two groups: (1) thiophenes and furans ($^1B_2 \le {}^1A_1$) and (2) selenophenes and tellurophenes ($^1A_1 < {}^1B_2$).[8] Since representatives of the both groups are characterized by a π-LUMO of the same type ($b^*{}_1$), it is evident that the change in the order of their appearance is caused by the rearrangement of the electron configurations in the ground state.[∧] For furan, thiophene, and tellurophene, this has been confirmed by photoelectron spectroscopy.[2]

One characteristic feature of the $\pi \to \pi^*$ transitions in chalcophenes, which is useful in practice, should be noted:[8–10] the $^1A_1 \to {}^1A_1$ transition is the most intense. UV spectra of divinyl chalcogenides (DVC) have been earlier discussed in Ref. 11. However, in contrast to chalcophenes, the spectral pattern for DVC is much more complex. Therefore, transition assignments for the electron spectra in Ref. 11 are only tentative.

In the present work, a more detailed study of the UV spectra of divinyl chalcogenides has been carried out. The behavior of vacant π^*-MO (in general case, π^* states) for a series of divinyl chalcogenides and chalcophenes has been considered.

Experimental

The compounds under study were synthesized by the methods described earlier.[12,13] According to GLC analyses, the purity of these compounds was better than 99.9 %. Electron absorption spectra were recorded on a Specord UV VIS spectrophotometer in heptane as a solvent (0.005–0.010 mol L^{-1}), $d = 0.0107$ cm. An optical cell 1 to 5 cm thick was used for recording gas-phase spectra.

Results and Discussion

UV absorption spectra of divinyl chalcogenides. Earlier[14] it was shown that transitions of three types appear in the UV spectra of gaseous alkyl vinyl chalcogenides: a low-energy transition from the $\pi \to np$, $\pi \to \pi^*$ Rydberg series and two transitions denoted as $\pi \to \sigma^*$. The energy gap between the maxima of the "σ" bands ($\Delta_\sigma{}^*$) is slightly dependent on the chain length and the structure

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[∧] Here, the order in which occupied MO of specific symmetry appear is referred to as the electron configuration.

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of alkyl radicals; it decreases somewhat as the atomic number of the halogen increases. These characteristics of the $\pi \rightarrow \sigma^*$ transitions could appreciably facilitate the band assignment in the absorption spectra of DVC providing some information on these transitions for the series $CH_2{=}CHXCH{=}CH_2$, $CH_3{-}CH_2XCH{=}CH_2$, and $CH_3{-}CH_2XCH_2{-}CH_3$ is available (the $\pi \rightarrow \sigma^*$ transitions for molecules of saturated compounds are actually identical to the $n_X \rightarrow \sigma^*$ transitions).

Unfortunately, only the long-wave bands of the $n_S \rightarrow \sigma^*$ transitions in saturated cyclic sulfides are known. They are of extremely low-intensity because of the symmetry exclusion.[15] For dialkyl sulfides, these bands are superimposed on an intense band arising from the $\sigma \rightarrow \sigma^*$ excitation.[15] Our analysis of the UV spectra of a wide variety of organyl chalcogenides showed that among those, organyl tellurides have some distinctive features. Two $n_{Te} \rightarrow \sigma^*$ transitions for dialkyl tellurides in the gas phase and in solution have an intensity that is sufficient to reliably identify them; the transitions appear in the longer-wave range than the $\sigma \rightarrow \sigma^*$ type transition (Table 1, Fig. 1). As can be seen from Table 1, the Δ^*_σ values for saturated and unsaturated tellurides differ insignificantly. Owing to this, the assignment of the absorption bands is simplified. The absence of intense Rydberg transitions in the UV spectra of gaseous divinyl sulfide and divinyl selenide also favors this assignment (Fig. 2).

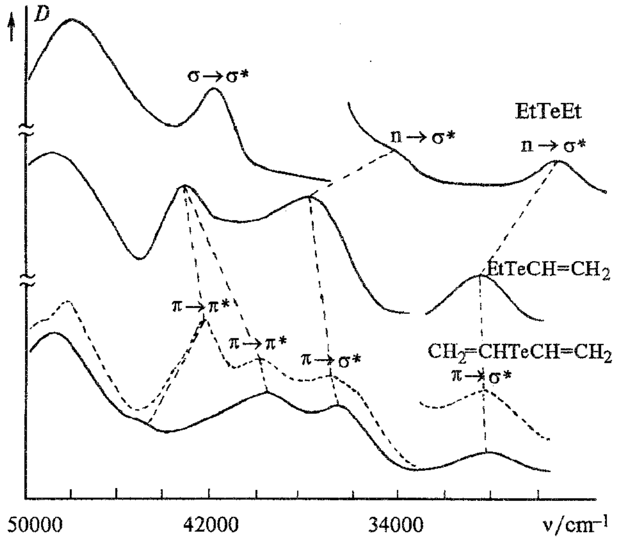

Fig. 1. UV spectra of organyl tellurides in a heptane solution. The dashed line is the spectrum of divinyl telluride in the gas phase.

Table 1. Energies of electron transitions in organyl chalcogenides

Compound	$\pi \rightarrow \sigma^{*a}$		$\Delta^*_\sigma = E^*_2 - E^*_1$	$\sigma \rightarrow \sigma^{*}$,[a]
	E^*_1/eV	E^*_2/eV	/eV	E^*_1/eV
		Heptane		
Pr^iTePr^i	3.41 (130)	4.25 (200)	0.84	5.21 (6800)
$Pr^iTeCH{=}CH_2$	3.72 (330)	4.63 (3500)	0.91	—
Bu^nTeBu^n	3.46 (90)	4.30 (180)	0.84	5.27 (5300)
$Bu^nTeCH{=}CH_2$	3.77 (360)	4.64 (4200)	0.87	—
MeTeMe	3.38 (90)	4.24 (150)	0.86	5.18 (5700)
$MeTeCH{=}CH_2$	3.75 (320)	4.67 (4800)	0.92	—
EtTeEt	3.42 (90)	4.29 (440)	0.87	5.24 (6800)
$EtTeCH{=}CH_2$	3.72 (450)	4.64 (4200)	0.91	—
$CH{=}CH_2TeCH{=}CH_2$	3.72 (460)	4.49 (4800)	0.77	—
$Pr^iSeCH{=}CH_2$	4.56 (2000)	5.66 (~2500)	1.10	—
$Bu^nSeCH{=}CH_2$	4.54 (2500)	5.70 (~3000)	~1.20	—
$EtSeCH{=}CH_2$	4.58 (1900)	5.70 (~2000)	~1.10	—
		Gas phase		
MeTeMe	3.36	4.23	0.87	*b*
$MeTeCH{=}CH_2$	3.76	4.79	1.03	—
EtTeEt	3.43	4.30	0.87	*b*
$CH{=}CH_2TeCH{=}CH_2$	3.77	4.58	0.81	—
$MeSeCH{=}CH_2$	4.66	5.70	~1.00	—
$EtSeCH{=}CH_2$	4.65	5.60	~0.9	—
$CH{=}CH_2SeCH{=}CH_2$	4.64	5.80	~1.20	—
$MeSCH{=}CH_2$	5.10	6.33	1.23	—
$CD_3SCH{=}CH_2$	5.13	6.33	1.20	—
$MeSCD{=}CD_2$	5.08	6.32	1.24	—
$Am^tSCH{=}CH_2$	4.98	6.27	1.29	—
$MeSCH{=}C{=}CH_2$	5.06	~6.25	~1.20	—
$CH_2{=}CHSCH{=}CH_2$	4.90	6.22	1.32	—

[a] Extinction coefficients are given in parentheses (ε/L mol^{-1} cm^{-1}).

[b] Superposition with a band of the Rydberg transition.

The second simplification stems from the following. It is known[16,17] that there is a linear relationship between the energies of the two highest occupied σ-MO in organyl chalcogenides. This relationship is acceptable for the two lowest unoccupied σ^*-MO, since in highly symmetric systems, these orbitals and the highest occupied σ-MO can be transformed by the identical irreducible representation. Indeed, the analysis of the UV spectra of organyl chalcogenides, in which both $\pi \to \sigma^*$ transitions are satisfactorily resolved (see Table 1), reveals a linear correlation in their energies. This correlation remains valid for all compounds under consideration regardless of the type of chalcogene and the number of unsaturated fragments (Fig. 3). Taking this into consideration, one can easily obtain the following energy relations for the electron transitions in DVC (see Tables 1 and 2): $\pi \to \sigma^* < \pi \to \sigma^* < \pi \to \pi^* < \pi \to \pi^*$ for Te and $\pi \to \sigma^* < \pi \to \pi^* < \pi \to \pi^* < \pi \to \sigma^*$ for S and Se.

The change in the Franck—Condon profile of the absorption curve for divinyl telluride as a function of the phase state (see Fig. 1) provides evidence that the shortwave $\pi \to \pi^*$ transition in the gas phase is superimposed on the $\pi \to n_S$ Rydberg transition. Of the $\pi \to \pi^*$ transitions in DVC, the short-wave transition is less intense (see Figs. 1 and 2). The great difference in intensities of the "σ" bands in divinyl telluride (see Fig. 1) can readily be explained if one assumes a planar conformation (C_{2v}) for this substance. For a nonplanar form (C_2) of DVC, the relation ^{1}A < ^{1}B corresponds to the excited π^* states. Since the ^{1}B state corresponds to electron configuration $a^2b^1b^*a^1$, and the positions of the orbitals with $a(a_2)$ symmetry are weakly dependent on the type of central atoms (see Table 2), there exists a nearly linear correlation (Fig. 4) between the energy

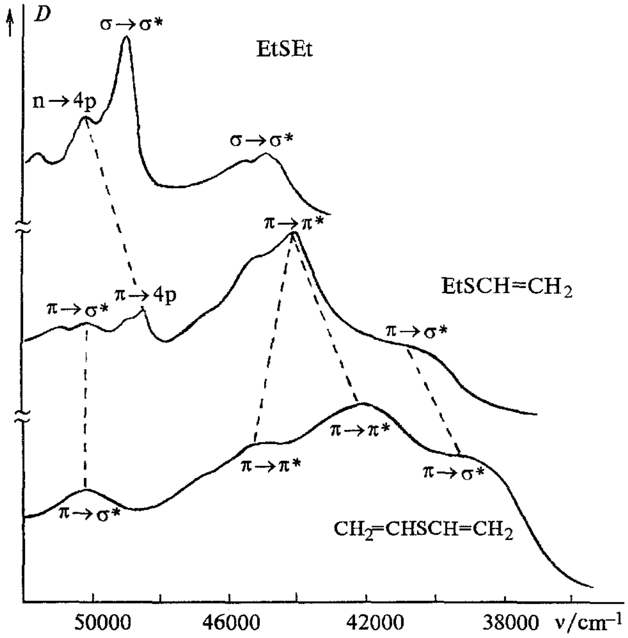

Fig. 2. UV spectra of organyl sulfides in the gas phase.

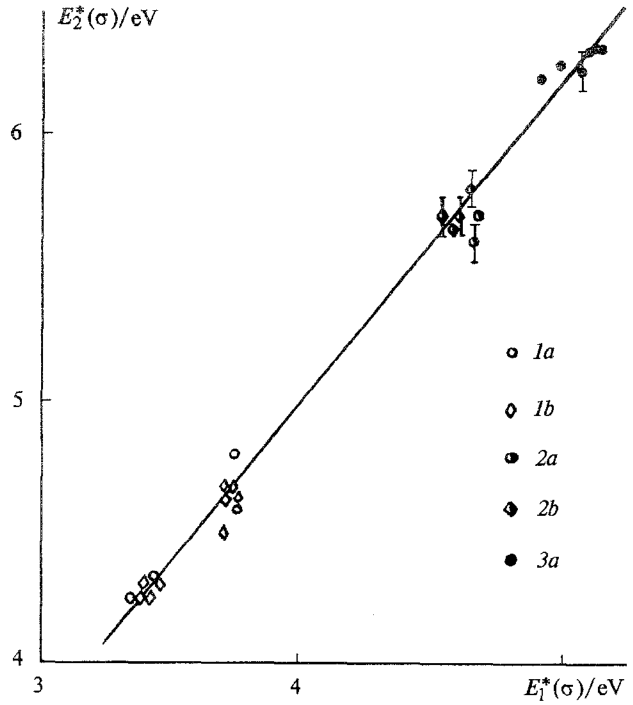

Fig. 3. Correlation between energies of the $\pi(n) \to \sigma^*$ transitions in the gas phase (*a*) and in a heptane solution (*b*): *1*, tellurides; *2*, selenides; *3*, sulfides.

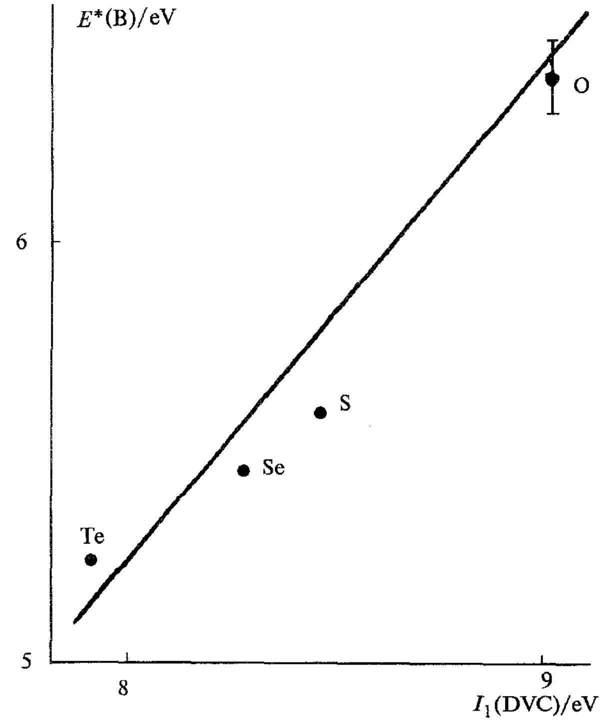

Fig. 4. Correlation between the energies of the ^{1}A → ^{1}B transition in divinyl chalcogenides in the gas phase and their first ionization potential.

Table 2. Electron characteristics of chalcophenes and divinyl chalcogenides

Compound	Energy of boundary π-MO,[a] E/eV				Excited state	Electron configuration	$E^*(\pi)$[b] /eV	$\frac{I+EA}{2}$ /eV	m[c] /eV
	a^2	b^2	b^*	a^*					
Furan	−8.89	−10.32	1.76	3.15	$^1A_1$	$b^1{}_1a^2{}_2b^1{}_1a^*{}_2$	6.10 (49200)[f]	6.04	0.06
					$^1B_2$	$b^2{}_1a^1{}_2b^1{}_1a^*{}_2$	5.88 (47400)[f]	5.33	0.55
Thiophene	−8.85	−9.50	1.15	2.63	$^1A_1$	$b^1{}_1a^2{}_2b^1{}_1a^*{}_2$	5.5 (~44000)	5.33	0.15
					$^1B_2$	$b^2{}_1a^1{}_2b^1{}_1a^*{}_2$		5.00	0.50
Selenophene	−8.81	−8.93	0.90	2.72	$^1A_1$	$b^1{}_1a^2{}_2b^1{}_1a^*{}_2$	5.03 (40600)	4.92	0.11
					$^1B_2$	$b^2{}_1a^1{}_2b^1{}_1a^*{}_2$	5.33 (42000)	4.86	0.47
Tellurophene	−8.84	−8.34	0.55	2.62	$^1A_1$	$a^2{}_2b^1{}_1b^1{}_1a^*{}_2$	4.51 (36400)[g]	4.45	0.06
					$^1B_2$	$a^1{}_2b^2{}_1b^1{}_1a^*{}_2$	5.20 (42000)[g]	4.70	0.50
3,4-Dimethyl-thiophene	−8.58	−8.94	1.1±0.2[d]	—	$^1A_1$	$b^1{}_1a^2{}_2b^1{}_1a^*{}_2$	5.24 (42300)		
					$^1B_2$	$b^2{}_1a^1{}_2b^1{}_1a^*{}_2$			
3,4-Диметил-selenophene	−8.34	−8.7	0.97±0.05[d]	—	$^1A_1$	$b^1{}_1a^2{}_2b^1{}_1a^*{}_2$	4.92 (39700)		
					$^1B_2$	$b^2{}_1a^1{}_2b^1{}_1a^*{}_2$	5.17 (41700)		
Divinyl ether	−10.5	−9.0	2.84[d]	2.8	^1A[e]	$a^2b^1b^1a^*$	6.02 (49080)		
					^1B	$a^2b^1b^*a^1$	~6.4 (sh, 51500)		
Divinyl sulfide	−10.36	−8.45	1.85[d]	1.71[d]	^1A	$a^2b^1b^1a^*$	5.25 (42320)		
					^1B	$a^2b^1b^*a^1$	5.58 (45000)		
Divinyl selenide	−10.26	−8.27	1.59[d]	1.63[d]	^1A	$a^1b^1b^1a^*$	5.03 (40600)		
					^1B	$a^2b^1b^*a^1$	5.45 (44000)		
Divinyl telluride	−10.05	−7.90	1.64[d]	1.58[d]	^1A	$a^2b^1b^1a^*$	4.87 (39920)		
					^1B	$a^2b^1b^*a^1$	5.24 (42280)		

[a] MO classification according to the C_2 point group. The orbital energies were determined by Coopmans theorem using literature data.[2,16,17] [b] Energies of π → π* transitions in the gas phase. Wavenumbers are given in parentheses. [c] For parameters in the DSD relation, see text. [d] Calculated by equation $EA = 2(E^* - m) - I$. [e] According to the C_2 point group, see text. [f] Literature data.[18] [g] Obtained from the spectrum in a heptane solution taking into account the phase shift in the spectra of other chalcophenes.

(E^*) of the $^1A \rightarrow {}^1B$ transition in DVC and the first ionization potentials of these compounds (I_1).

UV and PE spectra of selenophene. The separate consideration of the UV and PE spectra of selenophene stems from the fact that, although its UV spectrum agrees qualitatively with that of tellurophene (similar relations between band intensities and energy gaps for both substances), the PE spectrum of selenophene is characterized by a quasi-degenerate set of $\pi(b^2{}_1$ and $a_2{}^2)$-orbitals with the same order as that in thiophene ($a^2{}_2 \le b^2{}_1$). This implies that interpreting the UV and PE spectra in terms of simple notions would be contradictory. In this connection, the spectra of 3,4-dimethylselenophene (DMSP) are representative. There are two bands[16] in the PE spectrum of DMSP separated by a ~0.4-eV gap. However, the UV spectrum of DMSP differs from the spectrum of selenophene only in a small shift toward the red region (see Table 2), whereas the energy gap between the "π"-bands does not change significantly. A similar spectral pattern is characteristic of thiophenes, which have a substantial and unequal gap between the frontier π-MO in the ground state but, nonetheless, have a quasi-degenerate set of π* states (see Table 2).

Correlation of transition energies with ionization potential and electron affinity in chalcophenes. This problem was first discussed in Ref. 6 assuming that two occupied $\pi(a^2{}_2$ and $b^2{}_1)$-MO and one $\pi(b^*{}_1)$-LUMO are responsible for the long-wave π → π* transitions. This assumption was confirmed by a rough fit in the energy gaps in the PE and UV spectra. However, data that were interpreted differently[3,8] and later revised[7] were used for thiophene.[6] Actually, no such fit was found even for related substances (see above).

A comparison of the experimental values for I, EA, and $E^*(\pi)$ in the series of five-membered heterocycles (see Table 2) gives rise to a rather simple relationship: $E^* = m + (I + EA)/2$, where m is an energy parameter. If EA is constant, ΔE^* should be proportional to ΔI in agreement with the earlier assumption.[6] However, the DSD equation (DSD is doublet, singlet, and doublet) is obeyed only for those states, whose triple product of irreducible representations is fully symmetric (a peculiar selection rule). Thus, the energies of the excited $^1A_1$ states are almost exactly equal (m = 0.1 eV) to the arithmetic mean of the energies of the ionic $^2B_1$ states. For $^1B_2$, $^2B_1$, and $^2A_2$, m equals 0.5 eV (see Table 2). Hence, the DSD equation removes the contradictions

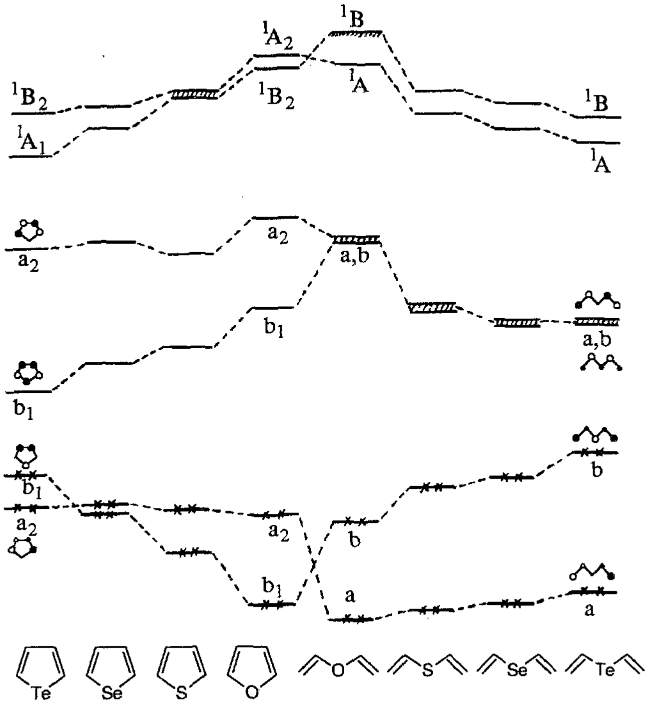

Fig. 5. Correlation diagram for energy levels of divinyl chalcogenides and chalcophenes.

noted above and corrects the simple orbital scheme. The estimates of electron affinity (EA_1) for model 3,4-dimethylchalcophenes in terms of the DSD equation using the known $E^*_{1,2}$ and $I_{1,2}$ values give rise to acceptable values and show that, even if a molecule has quasi-degenerate excited states, the mean error does not exceed 0.2 eV (see Table 2).

Electron affinity of divinyl chalcogenides. In contrast to chalcophenes, the long-wave $\pi \rightarrow \pi^*$ transitions in DVC are associated with one HOMO (b^2) and two LUMO (b^* and a^*). Consequently, one can estimate EA_1 and EA_2 for DVC (see Table 2). The EA_1 values for DVC are always smaller than those for the corresponding chalcophenes, whereas the reverse is true for EA_2. This tendency agrees fairly well with the structure of the π^*-MO in terms of Coopmans theorem (in acyclic structures, electron density on the bonding and antibonding portions of the C(3)—C(4) molecular orbitals is completely absent, Fig. 5). However, the mere fact that the π^*-MO are quasi-degenerate allows us to suggest that DVC molecules in the excited state are less planar than in the ground state. Variations in the torsion and bond angles (C—X—C) are possible upon excitation, though no independent data on such variations is known so far.

Correlation between π-MO and excited π* states. The correlation diagram between the energy levels and excited π^* states of chalcophenes and DVC (see Fig. 5) allows us to draw the following conclusions: (a) the energy positions of the $\pi(\pi^*)$-MO that can be transformed by irreducible representation b_1 depend mainly on the chemical structure of the substances under consideration; (b) there is a distinct tendency toward the opposite change in the energies of the $\pi(b^2{}_1)$- and $\pi^*(b^0{}_1)$-MO; (c) the energies of the excited π^* states, regardless of their symmetry, decrease as the atomic number of chalcogene increases; (d) for the $^1B_2$(^1B) states, this effect is related to a corresponding change in the energy of the $\pi^*(b^0{}_1)$-MO; (e) the energy of the $^1A_1$ (^1A) states varies mainly at the expense of the occupied $\pi^*(b^2{}_1)$-level; this is most distinctly seen in the case of DVC.

The last conclusion appears to reflect an appreciable difference in the contribution of the $\pi(b^2)$- and $\pi^*(b^0)$-MO to the electron population of chalcogene atoms, since a change in the atomic number of chalcogenes affects the energy of the occupied MO more strongly. In addition, when the C(3)—C(4) bond in chalcophenes is ruptured, again, the occupied $\pi(b^2)$-MO experiences stronger perturbation. As a result, DVC (X = O, S, Se) are characterized by an inverse order of occupied π-MO relative to chalcophenes (X = O, S, Se) and by a quasi-degenerate set of vacant MO (see Fig. 5). Thus, the excited states of chalcophenes and DVC (X = O, S, Se) cannot be described in terms of simple orbital schemes. Among the substances under discussion, only tellurophene and divinyl telluride have the same order of energies for excited π^* states and occupied and vacant π-MO.

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