Chemistry of Heterocyclic Compounds, Vol. 31, No. 1, 1995

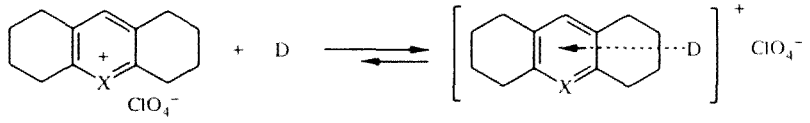
MOLECULAR COMPLEXES OF *sym*-OCTAHYDRO-1-CHALCOGENAANTHRACENE SALTS WITH AROMATIC COMPOUNDS

A. F. Blinokhvatov, O. V. Markovtseva, S. V. Chivokin, A. S. Archegova, N. T. Berberova, K. K. Kalnin'sh, and O. Yu. Okhlobystin*

Complexes of sym-*octahydro-10-chalocogenaanthracene perchlorates with aromatic hydrocarbons, di- and triatomic phenols, naphthols, and aromatic amines can be readily separated in the solid state. Complex formation is clearly shown to lower the oxidative power of the heteroaromatic cations.*

Formation of molecular complexes of chalcogenapyrilium salts with organic electron donors (D) is often observed in solution [1]. However, separation of these compounds in the solid state has previously been successful in only isolated cases [2, 3]. Possibly this was related to the use of sterically hindered 2,4,6-triaryl pyrilium and thiopyrilium salts. The plane of the aryl substituents in these forms an angle of 10-30° with that of the heterocycle [4] causing hindrance to an approach of donor and acceptor to a distance for effective intermolecular interaction.

We believe that this situation can be changed through use of the readily available *sym*-octahydro-10-chalcogenaanthracene perchlorates (I-III). These usefully differ from aryl substituted chalcogenapyrilium salts in a lower deviation from planarity and, according to electrochemical data [5], are not inferior in serving as electron acceptors. It was fund that salts I-III form colored complexes (IV-LIV, see Table 1) with naphthalene, anthracene, and a series of benzene derivatives. The majority of them are precipitated by combining concentrated acetone solutions of the components or when diluting these solutions with ether.



I-III IV-LIV

I X=O; II X=S; III X=Se

The highest (and nearest to quantitative) yields are achieved when using the thiopyrilium salt II as acceptor.

The slightly lower electron acceptor ability of pyrilium salt I when compared with II, III explains why their complexes with relatively weaker donors (phenylacetylene, naphthalene, phenols, and 4-nitroaniline) could not be separated in a crystalline state. In addition, while salt I does not co-precipitate from solution with 1-naphthol, it does for a good precipitate with 2-naphthol. This leads to a potential, practical isomer separation.

*Deceased.

Penza Agricultural Institute, Penza 440014. Science Research Institute for the Chemistry of Free Radicals, K. L. Khetagurov North Ossetian State University, Vladikavkaz 362040. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 27-32, January, 1995. Original article submitted November 22, 1994.

0009-3122/95/3101-0023$12.50

TABLE 1. Molecular Complexes IV-LIV

Acceptor	Donor	Molecular complex	Empirical formula	Color	Mp, °C	Yield, %
I	Phenylacetylene	IV*	$C_{21}H_{23}ClO_5$	Colorless	—	—
II		V	$C_{21}H_{23}ClO_4S$	Colorless	119...121	68
III		VI	$C_{21}H_{23}ClO_4Se$	Colorless	110...111	51
I	Naphthalene	VII*	$C_{23}H_{25}ClO_5$	Light yellow	—	—
II		VIII	$C_{23}H_{25}ClO_4S$	Light yellow	154...155	98
III		IX	$C_{23}H_{25}ClO_4Se$	Yellow	149...150	92
I	Anthracene	X	$C_{27}H_{27}ClO_5$	Light yellow	145...146	82
II		XI	$C_{27}H_{27}ClO_4S$	Orange-red	157...158	92
III		XII	$C_{27}H_{27}ClO_4Se$	Claret	149...150	92
I	Pyrocatechol	XIII*	$C_{19}H_{23}ClO_7$	Light yellow	—	—
II		XIV	$C_{19}H_{23}ClO_6S$	Light yellow	118...120	88
III		XV	$C_{19}H_{23}ClO_6Se$	Yellow	93...95	89
I	Resorcinol	XVI*	$C_{19}H_{23}ClO_7$	Light yellow	—	
II		XVII	$C_{19}H_{23}ClO_6S$	Light yellow	96...97	81
III		XVIII	$C_{19}H_{23}ClO_6Se$	Yellow	90...92	95
I	Hydroquinone	XIX*	$C_{19}H_{23}ClO_7$	Light yellow	—	—
II		XX	$C_{19}H_{23}ClO_6S$	Dark yellow	113...114	83
III		XXI	$C_{19}H_{23}ClO_6Se$	Yellow-orange	128...129	91
I	Pyrogallol	XXII*	$C_{19}H_{23}ClO_8$	Yellow	—	—
II		XXIII	$C_{19}H_{23}ClO_7S$	Dark yellow	123...124	81
III		XXIV	$C_{19}H_{23}ClO_7Se$	Dark yellow	119...120	93
I	1-Naphthol	XXV*	$C_{23}H_{25}ClO_6$	Light yellow	—	—
II		XXVI	$C_{23}H_{25}ClO_5S$	Dark yellow	156...157	90
III		XXVII	$C_{23}H_{25}ClO_5Se$	Yellow-orange	157...158	87
I	2-Naphthol	XXVIII	$C_{23}H_{25}ClO_6$	Light yellow	160...161	87
II		XXIX	$C_{23}H_{25}ClO_5S$	Dark yellow	178...179	95
III		XXX	$C_{23}H_{25}ClO_5Se$	Orange-brown	172...173	90
I	Aniline	XXXI	$C_{19}H_{24}NO_5$	Yellow	90...92	78
II		XXXII	$C_{19}H_{24}ClNO_4S$	Orange-red	110...111	84
III		XXXIII*[2]	$C_{19}H_{24}ClNO_4Se$	Red	—	—
I	4-Aminobenzoic acid	XXXIV	$C_{20}H_{24}ClNO_7$	Yellow	157...158	97
II		XXXV	$C_{20}H_{24}ClNO_6$	Orange	174...176	98
III		XXXVI	$C_{20}H_{24}ClNO_6Se$	Claret	163...164	96
I	4-Nitroaniline	XXXVII*	$C_{19}H_{23}ClN_2O_7$	Yellow	—	
II		XXXVIII	$C_{19}H_{24}ClN_2O_6S$	Dark red	112...113	96
III		XXXIX	$C_{19}H_{24}ClN_2O_6Se$	Yellow-orange	105...106	87
I	4-Aminoazobenzene	XL	$C_{25}H_{28}ClN_3O_5$	Yellow-orange	118...120	73
II		XLI	$C_{25}H_{28}ClN_3O_4S$	Dark red	100...102	80
III		XLII*[2]	$C_{25}H_{28}ClN_3O_4Se$	Dark red	—	—
I	2-Aminonaphthalene	XLIII	$C_{23}H_{26}ClNO_5$	Red	120...121	85
II		XLIV	$C_{23}H_{26}ClNO_4S$	Claret	125...126	91
III		XLV*[2]	$C_{23}H_{26}ClNO_4Se$	Dark claret	—	
I	1,8-Diaminonaphthalene	XLVI	$C_{23}H_{27}ClN_2O_5$	Dark violet	146...148	98
II		XLVII	$C_{23}H_{27}ClN_2O_4S$	Dark blue	156...158	99
III		XLVIII	$C_{23}H_{27}ClN_2O_4Se$	Blue-black	140...141	84
I	Diphenylamine	XLIX	$C_{25}H_{28}ClNO_5$	Yellow-orange	112...113	65
II		L	$C_{25}H_{28}ClNO_4S$	Dark red	106...108	77
III		LI	$C_{25}H_{28}ClNO_4Se$	Brown-violet	90...91	77
I	Carbazole	LII	$C_{25}H_{26}ClNO_5$	Light yellow	136...137	78
II		LIII	$C_{25}H_{26}ClNO_4S$	Yellow-orange	144...145	99
III		LIV	$C_{25}H_{26}ClNO_4Se$	Orange-red	134...135	97

*Not separated from solution.

*[2]Rapidly undergoes secondary reaction.

Separation of complexes of the selenopyrilium salt III with aromatic amines is complicated by rapid deprotonation processes because of the anomalously high mobility of the hydrogen atoms in the α,α'-methylene groups of the adjacent alicycles [6].

Detection of differences in the tendency of the *sym*-octahydro-10-chalcogenaanthracene salts to co-precipitate as complexes with weak electron donors leads to their potential use for the separation of complex mixtures. An additional factor supporting their use in this way is the quite ready fission of the complexes to the starting components. Slow introduction into their dilute solutions of ether causes precipitation of the uncomplexed acceptor.

TABLE 2. Position of the CT Band (ν_{CT}), Charge Transfer Energy ($E_{h\nu}$), Molecular Complex Formation Constant (K_{eq}), and Electron Affinity of the Cations (E_A)

Complex	Solvent	K_{eq}	ν_{CT}, cm^{-1}	$E_{h\nu}$, eV	E_A, eV)
X	$CHCl_3$	—	24320	3,01	5,57
XI	$CHCl_3$	—	23300	2,89	5,69
XII	$CHCl_3$	—	22000	2,72	5,86
X	CH_2Cl_2	—	21200	2,63	5,95
XI	CH_2Cl_2	1,32	20660	2,56	6,02
XII	CH_2Cl_2	17,72	20000	2,48	6,10
XLIII	CH_2Cl_2	6,36	21500	2,66	5,79
XLIV	CH_2Cl_2	10,68	21000	2,60	5,85
XLV	CH_2Cl_2	33,6	19500	2,41	6,04

TABLE 3. Electrochemical Parameters for the Molecular Complexes*

Complex	Solvent	$-E_{pk}^{comp}$, V	$-E_{pk}^{acc}$, V	ΔE_{pk}, V
X	CH_2Cl_2	0,813	0,767	0,046
XI	CH_2Cl_2	0,732	0,596	0,136
XII	CH_2Cl_2	0,573	0,496	0,077
X	$CHCl_3$	0,700	0,700	—
XI	$CHCl_3$	0,580	0,570	0,010
XIII	$CHCl_3$	0,340	0,430	—
XIX	CH_2Cl_2	0,791	0,767	0,024
XX	CH_2Cl_2	0,692	0,596	0,096
XXI	CH_2Cl_2	0,558	0,496	0,077
XLIII	CH_2Cl_2	1,075	0,767	0,208
XLIV	CH_2Cl_2	0,849	0,596	0,253
XLV	CH_2Cl_2	0,690	0,496	0,194
XLIX	CH_2Cl_2	1,011	0,767	0,244
L	CH_2Cl_2	0,879	0,596	0,283
LI	CH_2Cl_2	0,679	0,496	0,183

*$-E_{pk}^{comp}$) peak potential of the cathodic reduction of the molecular complex; $-E_{pk}^{acc}$) peak potential of the cathodic reduction of the free acceptor; $\Delta E_{pk} = E_{pk}^{comp} - E_{pk}^{acc}$.

All of the complexes, wit the exception of those in which the donors are volatile (phenylacetylene, aniline) or readily oxidized (pyrogallol, 1,8-diaminonaphthalene) are substances characterized by high stability and remain without signs of decomposition in the dark for a year. Calculation of their stability (K_{eq}) in solutio by the Benesi–Hildebrand method showed that the highest stability is associated with the selenopyrilium salt complex and the lowest with a pyrilium analog (see Table 2).

The low optical density of dilute solutions of complexes in the Charge Transfer (CT) band region explained why these new bands could be recorded only in the spectra of compounds X-XII and XLII-XLV. As was to be expected, the CT maxima underwent a bathochromic shift when going from oxygen to sulfur and to selenium complexes. The position of the CT band depends markedly on the polarity of the solvent used. Changing from chloroform to the less polar dichloromethane is accompanied by a shift of the CT maxima to the low frequency spectral region (2000-3120 cm^{-1}) corresponding to a 0.25-0.38 eV lowering of the CT energy ($E_{h\nu}$). The most marked effect of solvent change was seen for the pyrilium salt complexes I.

Using the known empirical equation $E_{h\nu} = I_D - E_A + 1.2$ eV [7], the calculated values of $E_{h\nu}$, and values of the donor first ionization potentials (I_D) the approximate values of the electron affinities (E_A) for the cationic salts I-III were found to be I: E_A = 5.57-5.95; II: E_A = 5.69-6.02; and III: E_A = 5.86-6.10 eV. The high values of E_A for the chalcogenapyrilium cations means that they can be considered as active one-electron oxidants.

Analysis of the vibrational spectra of all the separated complexes shows that complex formation is practically unrelated to the position of the characteristic acceptor absorption band in the region 1540-1620 cm^{-1} (ν heteroaromatic ring) but that it does cause a marked change in the spectral characteristics of the donor components.

Hence the typical phenylacetylene bands at 2115 (νC ≡ C) and 3300 cm^{-1} (νC−H) shift to low frequency by 90 and 50 cm^{-1} respectively. The spectra of resorcinol and hydroquinone differ in the complex state from those of the free samples by a high frequency shift of the hydroxyl group absorption band of 90 and 150 cm^{-1} respectively. For naphthols there is a similar but smaller shift of the hydroxyl group band in the same direction (25-50 cm^{-1}). By contrast, complex formation of pyrocatechol is accompanied by a hydroxyl band shift of 70-90 cm^{-1} to low frequency.

On the basis that the hydroxyl group absorption band shifts depend very little on the acceptor power of salts I-III it follows that the observed effect is due only to dissociation of the associated, uncomplexed donor molecules. This leads to weaker intermolecular and stronger intramolecular hydrogen bonds.

It was not possible to establish a characteristic effect for complex formation on change in the pattern of the vibrational spectra of the donors containing amino groups. The most significant changes were recorded when using 1,8-diaminonaphthalene. In place of the typical three amino group bands for this compound at 3280, 3300, and 3800 cm^{-1} the spectra of the complexes showed a single, intense band at 3350 cm^{-1}. At the same time there is noted a lowering in intensity for the acceptor absorption band. We could not rule out that these change were caused by a high degree of charge transfer. Confirmation is found from the presence in the EPR spectra of solid complex samples XLVI-XLVIII of singlet signals for the unpaired electrons with widths ΔH of 3.6 (XLVI), 2.0 (XLVII), and 4.7 mT (XLVIII).

The electrochemical data for these complexes was of some interest since it would allow determination of the effect of complex formation on chalcogenapyrilium salt reactivity in redox processes.

A study of the cathodic reduction of the complexes by cyclic voltammetry in dichloromethane showed that the effect of complex formation is clearly seen as a hindrance to the complex bound salt reduction when compared to the free salts (ΔE_{pk} 0.024 to 0.283 V, see Table 3). It should be noted that, for the majority of previously studied molecular complexes, the effect of complex formation is either not seen at all or is not very significant. Values of the change in component redox potentials have been reported in the range 0.02 to 0.08 V [8-13]. Surprisingly it was found that the changes in reduction potential values do not correlate with either the electron affinity of salts I-III or with the stability of the complexes formed by them.

It was also found that the effect of complex formation was not seen when using a solvent of high ionizing power (acetonitrile). We propose that a marked effect of complex formation on changes in reactivity of chalcogenapyrilium salts can be expected only when using low polarity solvents.

EXPERIMENTAL

IR Spectra were taken on a Specord 75-IR instrument using vaseline oil. Charge transfer bands in the complexes were recorded on a Specord M-40 instrument with dichloromethane solvent. EPR Spectra were taken on an Radiopan SEK/X-2543 radiospectrometer using a evacuated ampul ($4.5 \cdot 10^{-3}$ mm Hg).

Electrochemical measurements were made using an automated system consisting of a PI-50 pulsed potentiostat, PR-8 programmer, and Iskra-226 computer.

The working electrode was a platinum disk with area $6.25 \cdot 10$ cm^{-2}, the reference electrode saturated calomel with a water impermeable membrane, and the secondary electrode a platinum helix. The recording electrolyte was a 0.1 M solution of tetrabutylammonium perchlorate with a depolarizer concentration of $5 \cdot 10^{-3}$ molar.

Salts I-III were synthesized by known methods [14-16].

Elemental analytical data for the complexes obtained agreed with those.calculated.

Molecular Complexes (IV-LIX). These were mixed a solution of the salt I-III (0.001 mole) in acetone (2 ml) with a solution of the donor component (0.002 mole) in the minimum volume of acetone (phenylacetylene was used without solvent). The reaction mixture was diluted with ether (5-10 ml), and the crystalline precipitate was filtered off, washed with ether, and dried in a desiccator over calcium chloride.

REFERENCES

1. V. G. Kharchenko and S. N. Chalaya, Thiopyrans, Thiopyrilium Salts and Related Compounds [in Russian], Saratov University Publishers, Saratov (1987), p. 115.
2. J. A. Allan, I. C. Chang, L. F. Costa, and G. A. Reynolds, J. Chem. Eng. Data, **22**, 101 (1977).

3. B. H. Klandermann and D. C. Hoestrey, J. Chem. Phys., **51**, 377 (1969).
4. N. G. Bokii, R. V. Bedrinskii, V. V. Kitaev, N. A. Lopatina, and Yu. T. Struchkov, Koord. Khim., **2**, 103 (1976).
5. N. T. Berberova, A. F. Blinokhvatov, A. S. Archegova, E. S. Klimov, A. V. Shpakov, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 1, 47 (1991).
6. A. F. Blinokhvatov, N. N. Ivanova, and S. K. Klimenko, Khim. Geterotsikl. Soedin., No. 4, 463 (1993).
7. V. É. Kampar, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 5, 185 (1984).
8. Z. B. Chattopodhyay, M. N. Deshmukh, and C. J. Joce, J. Chem. Soc. Faraday Trans., No. 71, 1127 (1975).
9. L. Ramaley and S. Gaul, Canad. J. Chem., **56**, 2381 (1978).
10. R. L. Hasen, P. E. Toren, and R. H. Young, J. Phys. Chem., **70**, 1653 (1966).
11. I. P. Turovskis, Ya. P. Stradyn', J. Volke, Ya. F. Freimanis, and V. T. Glezer, Coll. Czech. Chem. Comm., 43, 909 (1978).
12. L. M. Baider, V. T. Glezer, and Ya. P. Stradyn', Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 3, 370 (1979).
13. V. T. Glezer, I. Ya. Kravis, Ya. P. Stradyn', Ya. F. Freimanis, and Ya. Ya. Dregeris, Izv. Akad. Nauk Latv SSR, Ser. Khim., No. 2, 225 (1979).
14. A. T. Balaban and N. S. Barbulescu, Rev. Roum. Chim., **11**, 109 (1966).
15. V. G. Kharchenko, S. K. Klimenko, and T. I. Krupina, Zh. Org. Khim., **3**, 1344 (1967).
16. A. F. Blinokhvatov, O. V. Markovtseva, I. A. Gleider, and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 5, 640 (1981).