

(AZA)DITHIAFULVALENES AS π -ELECTRON DONORS

R. GOMPPER* and R. GUGGENBERGER

Institut für Organische Chemie der Universität München
Karlstraße 23, D-8000 München 2

(Received in Germany 24 September 1985)

Abstract- (Aza)1,2- and 1,4-dithiafulvalenes are more difficult to oxidize than tetrathiafulvalenes. Depending on substituents, (aza)dithiafulvalenes react with tetracyano-p-quinodimethane (TCNQ) either in a 1:1 or 2:3 ratio to form heterofulvalenium 7,7,8,8-tetracyano-p-quinodimethanides. The electrical conductivity of these salts strongly depends on substituents. The conductivities of alkylthiofulvalene-TCNQ salts are much higher than those of phenyl-substituted derivatives.

In preceding papers^{1,2}, the synthesis of new heterofulvalenes isoelectronic with sesquifulvalenes has been reported. Our plan was to design novel π -donors that could be used for the preparation of new charge transfer complexes or radical-cation salts. Since compounds of the sesquifulvalene series are expected to be weaker π -donors than those of the heptafulvalene series, compounds with electron-releasing groups were prepared. These groups could also help to counterbalance the electron-withdrawing effect of ring N-atoms.

Electrochemical studies

The formation of charge transfer complexes and cation/anion-radical salts depends on the redox potentials of the donor and acceptor components.³ Information about the donor properties of our new (aza)dithiafulvalenes was gained through cyclic voltammetry (cf. Table 1). The dithiafulvalenes studied here are more difficult to oxidize than tetrathiafulvalene (TTF) and bis-ethylendithio-tetrathiafulvalene (BEDT-TTF) and are for that matter more related to tetra-kis-methylthio-ethylene (9) than to TTF. All processes were found to be irreversible. The position of the maxima of irreversible electron transfer reactions depends, *inter alia*, on the sweep-rate (v). In order to rule out the influence of the sweep-rate the potential of the peak current (I_p) was measured at various sweep rates. Since $I_p \sim \sqrt{v}$, extrapolation to $v = 0$ gives reproducible oxidation potentials $E_{p,ox}$ (cf. Table 1; standard error ± 15 mV). In contrast to the reactions described in this paper, the oxidations of TTF⁴ and BEDT-TTF⁵ are reversible and lead to rather stable radical cations.

Table 1 Oxidation potentials ($E_{p_{ox}}$) of dithiafulvalenes 1², 2¹, 3⁶ and related compounds (vs. SCE)

	$E_{p_{ox}}\text{ (V)}$		$E_{p_{ox}}\text{ (V)}$
	0.57		0.82
	0.70		0.92
	0.72		0.90
	0.98		1.00
	0.33 ⁴		0.83 ⁷
	0.53 ⁵		-0.75 ⁸

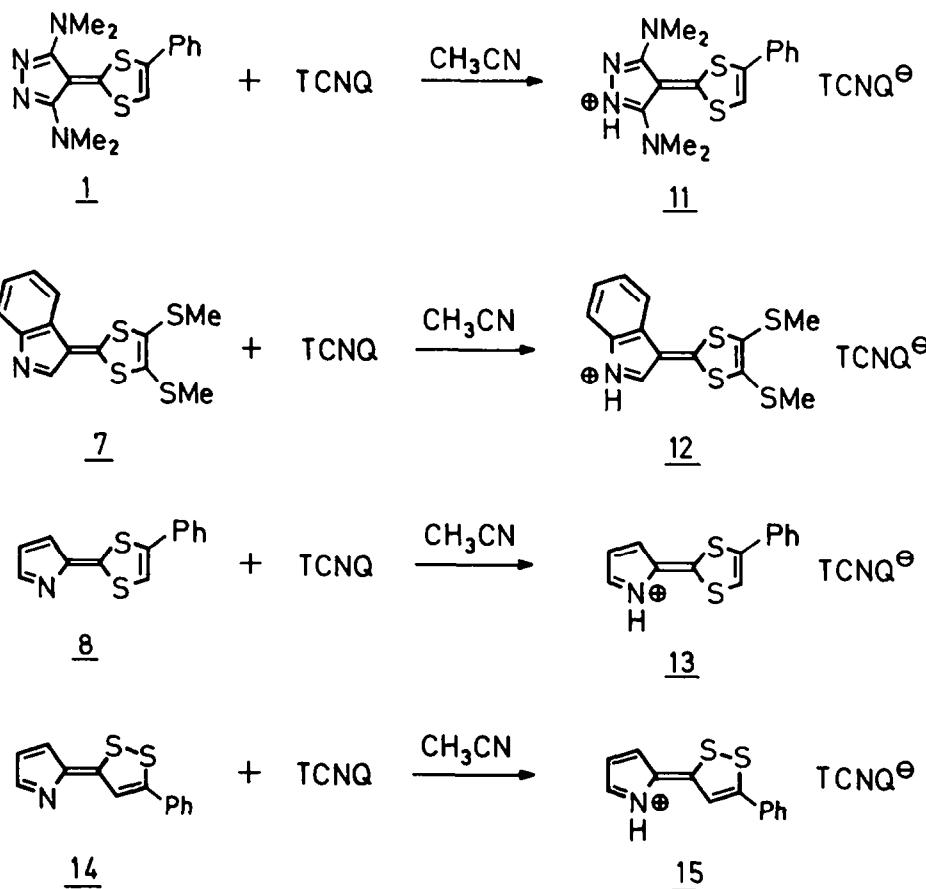
The oxidation potentials of 1-9 depend strongly on substituents. Most difficult to oxidize is 8 that bears no donor substituents. Methylthio groups only slightly lower the oxidation potential (cf. 6 vs 8 and 3 vs 5). Interestingly

enough, in the TTF series alkylthio groups even raise the oxidation potential (cf. BEDT-TTF vs TTF). Still, BEDT-TTF can be readily oxidised to radical cation salts whose electrical conductivities are even more interesting than those of TTF radical cation salts.^{5,9} The 1,4-dithia-6,7-diaza-fulvalene 1² has the lowest oxidation potential of 1-8 and is closest in this property to BEDT-TTF. Obviously, dimethylamino groups act as stronger donors than methylthio groups as is demonstrated further when 10 is compared with 9.

Reactions of azadithiafulvalenes with TCNQ and bromine

TCNQ^{10,11} is of particular importance as an acceptor molecule in charge transfer complexes. There are four groups of TCNQ complexes with donor molecules: (1.) 1:1 charge transfer complexes having low electrical conductivities (cf. pyren-TCNQ; ref. 11). (2.) Complexes displaying partial charge transfer and high electrical conductivities (cf. TTF-TCNQ; ref. 12). Characteristically, these complexes crystallize in separate stacks of the donor and acceptor components which seems to be essential for a high conductivity (ref. 13,14). (3.) Salts of TCNQ radical anions with inorganic or organic cations (cf. N-methylquinolinium tetracyanoquinodimethanide; ref. 11). As a result of the complete charge transfer the conductivities of these salts are mostly rather low (ref. 11). (4.) Complexes containing TCNQ besides TCNQ radical anions. Their electrical conductivities are higher than those of the complexes of group 3 (cf. N-methylquinolinium tetracyanoquinodimethanide \times 0.5 TCNQ; ref. 11).

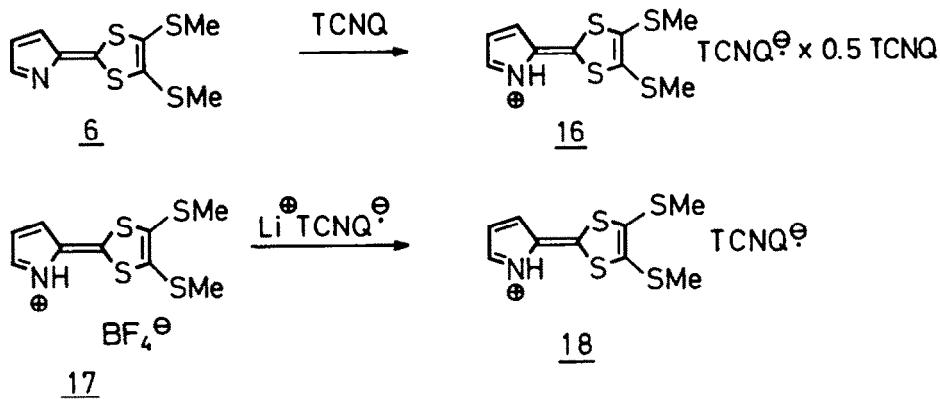
TCNQ reacts with 1, 7, 8 and 14 in hot acetonitrile (method A) to furnish the salts 11-13 and 15 consisting of protonated fulvalenes and TCNQ radical anions. These salts that belong to group 3 are also produced from fulvalene perchlorates/tetrafluoroborates^{1,6} and lithium TCNQ (method B). Although the



appearance of the compounds obtained by the two methods is somewhat different (A: black crystal powders, B: bluish-black needles) the elemental analyses are virtually the same. This does not exclude radical cation salts, however, since the calculated values for both types of salts are within the limits of the method. The IR spectra display only poorly resolved bands. The UV/VIS spectra (cf. Table 3) show long-wavelength absorption maxima characteristic for TCNQ radical anions and moreover the maxima of the protonated fulvalenes. Maxima of radical cations expected to appear between 500 and 800 nm¹⁵ are not apparent. The electrochemical behavior of 11-13 and 15 is in accord with the structures given. The presence of traces of charge transfer complexes in the products obtained by method A cannot be excluded, however. The maximum at 394 nm has a distinctly higher extinction coefficient than that in the salts prepared by method B where it appears only as a shoulder as in lithium TCNQ. This indicates the presence of small amounts of TCNQ in the salts resulting from method A. In addition, the spectra of these salts at the maximum of 845 nm, typical for the TCNQ radical anion,¹¹ show a lower intensity.

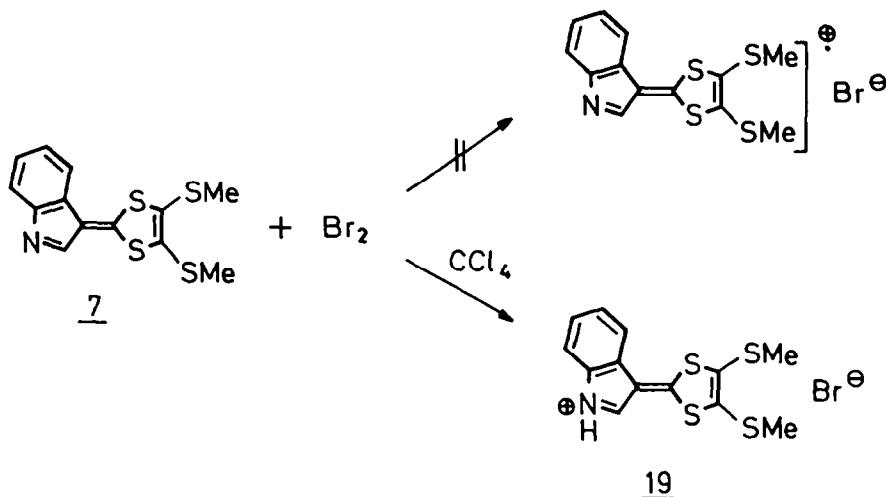
The formation of the salts 11-13 and 15 instead of radical cation salts is in accordance with the reaction of TCNQ with numerous amines which leads to ammonium salts¹¹ (in reactions of some azadithiafulvalenes with dichlorodicyano-p-benzoquinone and TCNQ the formation of radical cation salts has been claimed¹⁶).

In contrast to the reactions of 1, 7, 8 and 14 with TCNQ which afford the same salts as the reactions of fulvalenium perchlorates with lithium TCNQ, the



product 16 formed when 6 reacts with TCNQ is different from the salt 18 produced from the reaction of tetrafluoroborate 17 of 6 with lithium TCNQ. Elemental analysis of 16 and the strong absorption maximum at 394 nm ($\lg \epsilon = 4.76$) in the UV/VIS spectrum (cf. Table 3) indicate the presence of neutral TCNQ in 16.

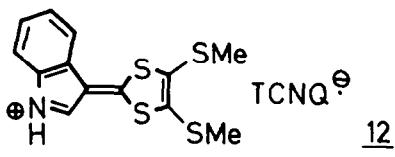
The reaction of the fulvalene 7 with bromine takes the same course as that of 7 with TCNQ. Instead of a radical cation bromide the hydrobromide 19 of 7 is formed. The ESR spectrum of 19 displays only a very weak signal indicating a spin concentration of 1.2×10^{-18} unpaired electrons/gram, obviously caused by an impurity.



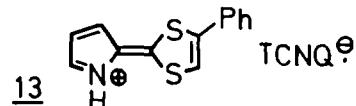
Electrical conductivities

The pellet conductivities of 12, 13, 16 and 19 are listed in Table 2. In view of the fact that single-crystal conductivities normally are roughly 10^2 times higher than those of powders, the pellet conductivities of 12 and 16 are

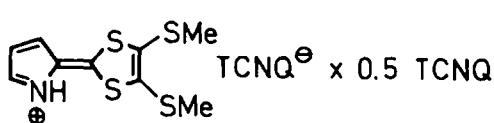
Table 2 Electrical pellet conductivities ($p = 1800 \text{ kp/cm}^2$, 2-electrode probe) of 12, 13, 16 and 19



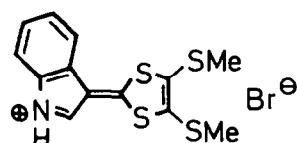
$$\begin{array}{ll} \text{method A} & 8.3 \times 10^{-3} \text{ S/cm} \\ \text{method B} & 6.2 \times 10^{-4} \text{ S/cm} \end{array}$$



$$5.6 \times 10^{-12} \text{ S/cm}$$



$$1 \times 10^{-4} \text{ S/cm}$$



$$1 \times 10^{-7} \text{ S/cm}$$

remarkably high. The fact that the conductivity of 12 depends to some extent on the method of preparation (A or B) is in line with the assumption that the material obtained by method A contains a small amount of charge transfer com-

plex or radical cation salt. The conductivity of salt 19 points in the same direction.

The extremely low conductivity of 13 as compared with the conductivities of 12 and 16 demonstrates that the phenyl group sterically hinders the formation of separate stacks.

Conclusion

Cyclic voltammetry of dithiafulvalenes and azadithiafulvalenes reveals that these compounds which are isoelectronic with sesquifulvalene are more difficult to oxidize than the heptafulvalene derivatives TTF and BEDT-TTF. Donor substituents such as methylthio groups obviously cannot counterbalance the weaker electron donor properties of the sesquifulvalene system, as compared with the heptafulvalenes, and the electron-withdrawing effect of ring nitrogen atoms. TCNQ reacts with azadithiafulvalenes to afford salts consisting of heterofulvalenium cations and TCNQ radical anions. In one case a salt was obtained that contains TCNQ besides TCNQ radical anion. The electrical conductivities of these salts are in the range of 10^{-12} - 10^{-2} S/cm. Methylthio group cause much better conductivities than phenyl groups.

Experimental

IR spectra were determined on Perkin-Elmer 125 and 157 spectrophotometers, UV/VIS spectra on a Zeiss DMR 10 spectrometer. Electrochemical oxidations were performed with a Bioanalytical Systems Cyclic Voltammeter CV 1B ($c = 10^{-3}$ M in acetonitrile, 0.1 M Et_4NBF_4 , Ag/AgCl as the reference electrode). Melting points were determined on a Büchi SMP-20 apparatus and are uncorrected.

General procedures for the preparation of azafulvalenium-tetracyano-p-quino-dimethanides 11-13, 15. 2-(3-Indolyl)-4,5-bis-methylthio-1,3-dithiolium-7,7,8,8-tetracyano-p-quinodimethanide (12). Method A: To the boiling solution of 0.41 g (2 mmol) TCNQ in 20 ml acetonitrile was added the solution of 0.62 g (2 mmol) 7 (ref. 1) in 20 ml acetonitrile and the mixture kept at room temperature for 1 day. The precipitate was then isolated by filtration and recrystallized from acetonitrile to afford 0.60 g (58%) of a black powder, mp 208-213°C (dec.). Anal. Calcd for $\text{C}_{25}\text{H}_{16}\text{N}_5\text{S}_4$ (514.7): C, 58.34; H, 3.13; N, 13.61; S, 24.92. Found: C, 58.30; H, 3.26; N, 13.38; S, 24.92. Method B: To the solution of 0.45 g (1.13 mmol) 7-tetrafluoroborate (ref. 1) in 10 ml hot acetonitrile the solution of 0.24 g (1.13 mmol) lithium TCNQ in 10 ml water was added. After 2 h the precipitate was collected by filtration and recrystallized from acetonitrile to afford 0.55 g (95%) dark green needles, mp 176-177°C (dec.). Anal. Found: C, 58.32; H, 3.21; N, 13.46; S, 24.72.

2-(3,5-Bis-diethylamino-4-pyrazolyl)-4-phenyl-1,3-dithiolium-7,7,8,8-tetracyano-p-quinodimethanide (11). A: 0.28 g (52%), black needles, mp 243°C (dec.). Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{N}_8\text{S}_2$ (535.7): C, 62.78; H, 4.33; N, 20.92 S, 11.97. Found: C, 62.73; H, 4.44; N, 20.83; S, 11.98. B: 0.93 g (75%), violet needles, mp 248-250°C (dec.). Anal. Found: C, 63.05; H, 4.50; N, 20.87; S, 12.01.

4-Phenyl-2-(2-pyrrolyl)-1,3-dithiolium-7,7,8,8-tetracyano-p-quinodimethanide (13). A: 1.1 g (49%), green-black powder, mp 198-202°C (dec.). Anal. Calcd for $\text{C}_{25}\text{H}_{14}\text{N}_5\text{S}_2$ (448.5): C, 66.95; H, 3.15; N, 15.61; S, 14.30. Found: C, 67.19; H, 2.81; N, 15.65; S, 14.92. B: 0.30 g (67%), bluish-black crystals, mp 193-195°C (dec.). Anal. Found: C, 67.02; H, 3.17; N, 15.35; S, 14.30.

5-Phenyl-3-(2-pyrrolyl)-1,2-dithiolium-7,7,8,8-tetracyano-p-quinodimethanide (15). A: 0.30 g (67%), black powder, mp 190°C (dec.). Anal. Calcd for $\text{C}_{25}\text{H}_{14}\text{N}_5\text{S}_2$ (448.5): C, 66.95; H, 3.15; N, 15.61; S, 14.30. Found: C, 66.97; H, 3.02; N, 15.67; S, 14.33. B: 0.30 g (46%), black needles, mp 189°C (dec.). Anal. Found: C, 67.18; H, 3.41; N, 15.61; S, 14.30.

4,5-Bis-methylthio-2-(2-pyrrolyl)-1,3-dithiolium-7,7,8,8-tetracyano-p-quinodimethanide x 0.5 TCNQ (16). A: 0.60 g (35%), dark green platelets, mp 174°C (dec.). Anal. Calcd for $\text{C}_{27}\text{H}_{16}\text{N}_7\text{S}_4$ (566.7): C, 57.33; H, 2.67; N, 17.33;

S, 22.67. Found: C, 57.32; H, 2.90; N 17.15; S, 22.80.

4,5-Bis-methylthio-2-(2-pyrrolyl)-1,3-dithiolium-7,7,8,8-tetracyano-p-quino-dimethanide (18). B: 0.40 g (86%), green needles, mp 171-172°C (dec.). Anal. Calcd for $C_{21}H_{14}N_5S_4$ (464.6): C, 54.31; H, 3.04; N, 15.08. Found: C, 53.78; H, 3.19; N, 14.84.

2-(3-Indolyl)-4,5-bis-methylthio-1,3-dithiolium-bromide (19). a) To the warm solution of 0.62 g (2 mmol) 7 (ref. 1) in 40 ml carbon tetrachloride was added dropwise the solution of 0.16 g (1 mmol) bromine in 10 ml carbon tetrachloride. The precipitate formed after 3 h was collected by filtration and recrystallized from acetonitrile to afford 0.65 g (83%) of a dark red powder, mp 231-233°C (dec.). Anal. Calcd for $C_{13}H_{12}BrNS_4$ (390.4): C, 40.00; H, 3.10; N, 3.59;

S, 32.85. Found: C, 39.84; H, 3.12; N, 3.31; S, 32.68. b) To the suspension of 0.62 g (2 mmol) 7 in 10 ml acetonitrile was added 0.41 g (2.2 mmol) 48% hydrobromic acid. The black precipitate was collected by filtration and washed with acetonitrile to afford after drying 0.70 g (90%) of a dark red powder, mp 244°C (dec.).

Table 3 Spectroscopic data of 11-13, 15, 16, 18 and 19

method		IR (KBr) ν (cm $^{-1}$)	UV/VIS (CH $_3$ CN)	
				λ_{max} , nm (lg ϵ)
<u>11</u>	A	2170	845 (4.52), 820 (4.34), 761 (4.15), 743 (4.23), 727 (4.01), 698 (3.67), 680 (3.70), 665 (3.59), 421 (4.59), 394 (4.90), 280 (3.75), 227 (4.37).	
	B	3180 2180 2150	845 (4.68), 820 (4.50), 760 (4.33), 743 (4.40), 727 (4.20), 697 (3.90), 680 (3.92), 665 (3.84), 433 (4.50), 407 (4.71), 394 (4.66), 279 (3.89), 227 (4.47).	
<u>12</u>	A	2180	845 (4.66), 820 (4.66), 760 (4.34), 742 (4.41), 726 (4.20), 695 (3.92), 679 (3.94), 665 (3.07), 476 (4.56), 436 (4.50), 421 (4.54), 406 (4.53), 394 (4.52), 281 (4.27), 252 (4.27), 216 (4.75).	
	B	2190 2180 2165 2150	845 (4.67), 820 (4.49), 760 (4.34), 742 (4.41), 726 (4.20), 698 (3.93), 679 (3.94), 667 (3.86), 464 (4.44), 436 (4.56), 422 (4.57), 408 (4.51), 395 (4.43), 304 (4.11), 280 (3.98), 250 (4.11), 234 (4.28).	
<u>13</u>	A	2175 2145	845 (4.37), 820 (4.17), 760 (4.05), 743 (4.12), 725 (3.92), 680 (3.63), 664 (3.56), 442 (4.55), 422 (4.48), 394 (4.71), 373 (4.49), 240 (4.22).	
	B	2180 2145	840 (4.56), 820 (4.40), 761 (4.25), 743 (4.32), 725 (4.10), 680 (3.94), 664 (3.70), 450 (4.68), 440 (4.70), 425 (4.61), 410 (4.50), 395 (4.41), 315 (3.74), 280 (3.75), 245 (4.30), 235 (4.28).	
<u>15</u>	A	2190	845 (4.28), 820 (4.12), 761 (3.97), 742 (4.05), 725 (3.89), 680 (3.61), 662 (3.52), 530 (3.85), 495 (4.06), 455 (4.32), 438 (4.39), 420 (4.39), 394 (4.62), 376 (4.47), 272 (3.82), 233 (4.06).	
	B	2180	843 (4.46), 820 (4.30), 760 (4.13), 742 (4.20), 727 (4.00), 700 (3.70), 678 (3.72), 666 (3.64), 457 (4.47), 437 (4.49), 422 (4.46), 406 (4.48), 394 (4.51), 372 (4.39), 276 (3.90), 232 (4.09).	
<u>16</u>	A	2170	843 (4.66), 820 (4.49), 760 (4.32), 743 (4.39), 726 (4.20), 696 (3.93), 680 (3.94), 665 (3.88), 474 (4.45), 436 (4.47), 419 (4.55), 394 (4.76), 375 (4.59), 302 (3.86), 278 (3.82), 250 (4.13), 233 (4.19).	
<u>18</u>	B	3160 2195 2178 2151	843 (4.62), 820 (4.46), 760 (4.30), 743 (4.37), 727 (4.17), 696 (3.90), 680 (3.01), 665 (3.84), 472 (4.44), 436 (4.47), 420 (4.51), 406 (4.47), 395 (4.44), 305 (3.88), 278 (3.84), 250 (4.11), 233 (4.17).	
<u>19</u>		2960, 2805 1500, 1410	475 (4.40), 354 (3.40), 282 (4.02), 250 (4.00).	

Acknowledgements- This work has been funded by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Electrical conductivities and ESR spectra have been measured by Dr. J. Hocker, Bayer AG, Leverkusen. Part of the cyclovoltammetry has been carried out by Dr. K. H. Grosse Brinkhaus, Institut für Organische Chemie der Universität Bonn.

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