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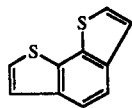
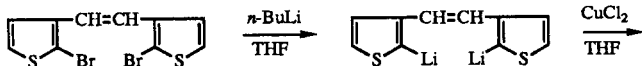
The photochemical behaviour of *cis* and *trans* 1,2-bis(2-bromo-3-thienyl)ethene has been separately studied with respect to cyclization to benzo[2,1-*b*:3,4-*b'*]dithiophene (BDT). The *gc/ms* analysis of the mother liquors of the two isomers photoreaction shows the opposite direction of isomerization followed by production of intractable materials resulting by the radical breaking of one of the two C-Br bonds on the thiophene moiety. On the contrary, in EI mass spectrometry both the isomers give rise to fragment ions at *m/z* 190 studied and compared to BDT with the aid of mass analysed ion kinetic energy spectrometry and collisional spectroscopy.

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Introduction.

In recent years the interest in conductive polymers has strongly increased, due to their possible application in electrochromic devices, batteries [1] and electronic materials [2]. For these reasons, researches are currently devoted to the individualization of possible monomeric units to be used for electrochemical polymerization [3]. In this contest, benzo[2,1-*b*:3,4-*b'*]dithiophene (BDT) (**1**) appears to have suitable characteristics because the position to the sulfur atom represents the more reactive center leading to no branched and aromatic polymer with marked conductive performances. The BDT synthesis already has been described in the literature [4] using *cis*- and *trans*-1,2-bis(2-bromo-3-thienyl)ethenes **2** and **3** as parent compounds (Scheme 1). Concerning the hypothesis that the chemical cyclization is possible only starting from the *cis* isomer, we preferred to separate the ethene mixture (65% *cis* and 35% *trans*). This separation was accomplished by means of flash column chromatography on Kiesegel 60 (Merck) 70-230 mesh using hexane as eluent. The two isomers (*cis* mp 48° and *trans* mp 147°) were characterized by ¹H-nmr spectroscopy (Figure 1a and 1b).

Scheme 1



We tried to perform the ethene cyclization employing radicals instead of anions by a photochemical reaction. Both isomers were separately irradiated through a quartz vessel with a 125 W medium pressure mercury lamp [4] and both failed to yield the cyclization product BDT. Irradiation of the *trans* isomer **3** produced at first a little isomerization to the *cis* isomer, then both of the isomers lead to intractable materials. With respect to *cis* isomer **2** photoreaction, the *gc/ms* analysis showed a large *cis-trans* isomerization with establishment of a photostationary state: 95% *trans*, 5% *cis* and intractable materials being the main product of the reaction. However, some other side-products were detected by mass spectrometry, after three hours, in a very small amount in the photo-irradiated solution. As it is shown in Table 1, the formulae of these products fit well with substituted 1,2-bis(3-thienyl)ethene structure, on which radicals present in solution, *e.g.* chlorine, iodine or oxygen, have replaced one bromine atom. From these results we can infer that photolysis produces two different processes: the ethene double bond isomerization to the more stable *trans* isomer and the radical breaking of one of the two C-Br bonds on the thiophene moiety. Study the photochemical behaviour of 1,2-di(3-thienyl)ethene Kellogg *et al.* [5] proposed the formation of a transitory dihydro intermediate which cannot be oxidized to BDT. In compound **2** the hindrance of two bromine atoms inhibits the formation of such an intermediate. Moreover, the opposite direction of the isomerization we observed (*cis trans* against *trans cis*) can be explained by the lack of such driving force. The cyclization products could originate only from the abstraction of two bromine radicals from **2** followed by the ring closure of the

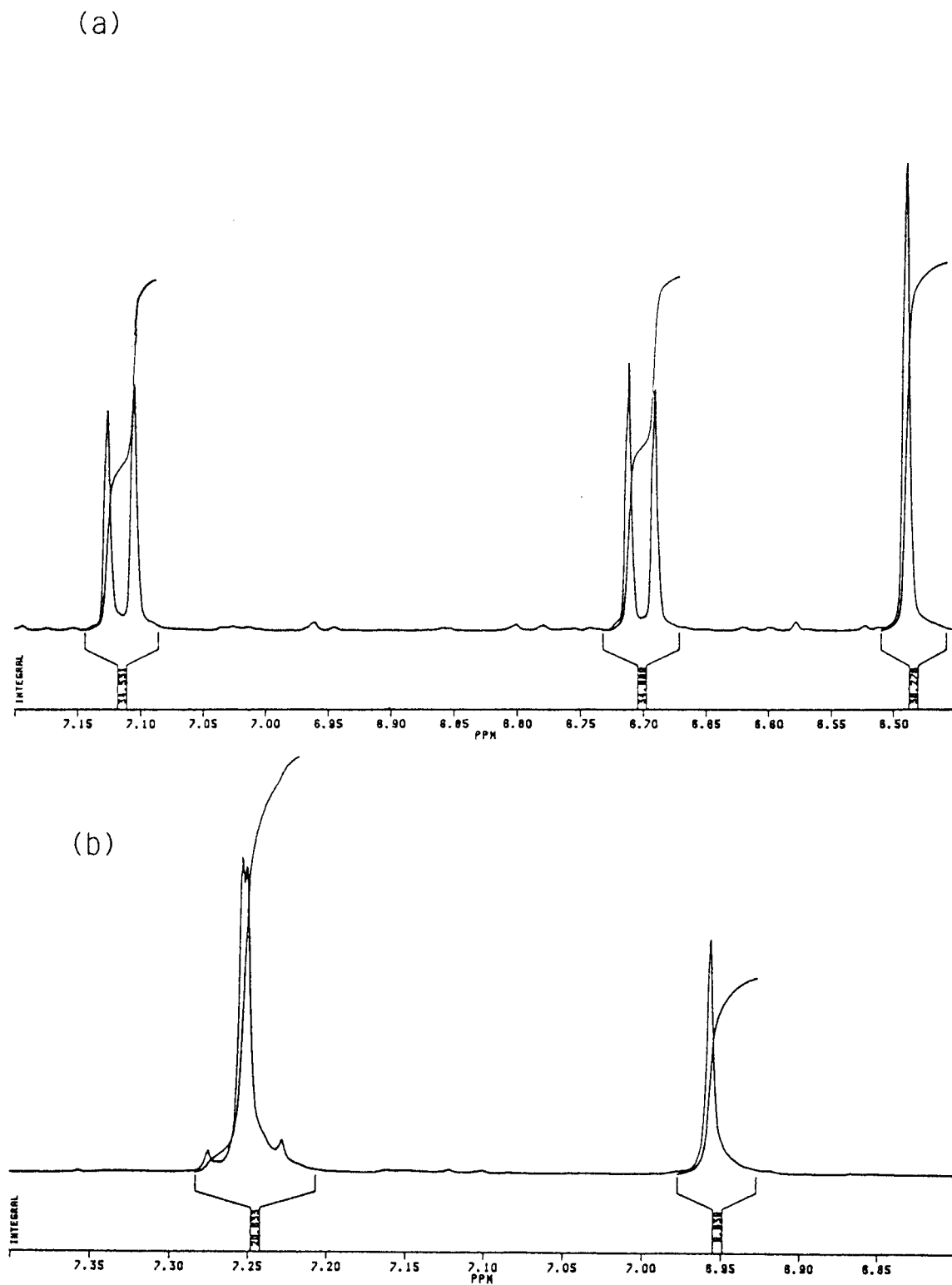


Figure 1. ¹H-nmr spectra of a) compound 2 and b) compound 3.

intermediate compound(s). The very small amount of BDT demonstrates that the energy involved in the photolysis process is not sufficient to extract two bromine atoms. The *cis* and *trans* isomers were analyzed by EI mass spectrometry (70 eV, 200 μ A and 200 $^\circ$) employing a VG ZAB2F instrument. In particular, mass analyzed ion kinetic energy spectra (MIKES) of M^+ from **2** and **3** isomers gave interesting results as shown in Figure 2. The only primary decomposition pathways are due to unimolecular losses of Br and 2 Br (Scheme 2).

Scheme 2

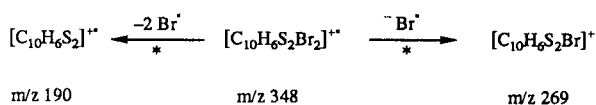


Table 1

Qualitative and Quantitative Data from GC-MS Analysis of Reaction mixture Arising from Photolysis of Compounds 2

Photolysis time (minutes)	254	188	190	348	304	285	348	396	346
30				57			43		
90				40	1.1	1.2	92.5	1.2	
180	0.3	1.3	--	1.5	2.7	1.2	87.7	4.6	0.7
240	0.5	2.1	--	1.0	1.9	1.2	90	2.6	0.7
420	0.5	2.4	0.2	1.1	1.9	2.0	88.6	2.6	0.7
Residue	0.6	2.1	1.7	1.0	1.8	2.0	88.5	1.7	0.6

Elemental formulae as derived from ms	$C_5H_4SBr_2$	$C_{10}H_4S_2$	$C_{10}H_6S_2$ BDT	$C_{10}H_6S_2Br_2$ <i>cis</i>	$C_{10}H_6S_2BrCl$	$C_{10}H_8NS_2Br$	$C_{10}H_6S_2Br_2$ <i>trans</i>	$C_{10}H_6S_2BrI$	Unknown
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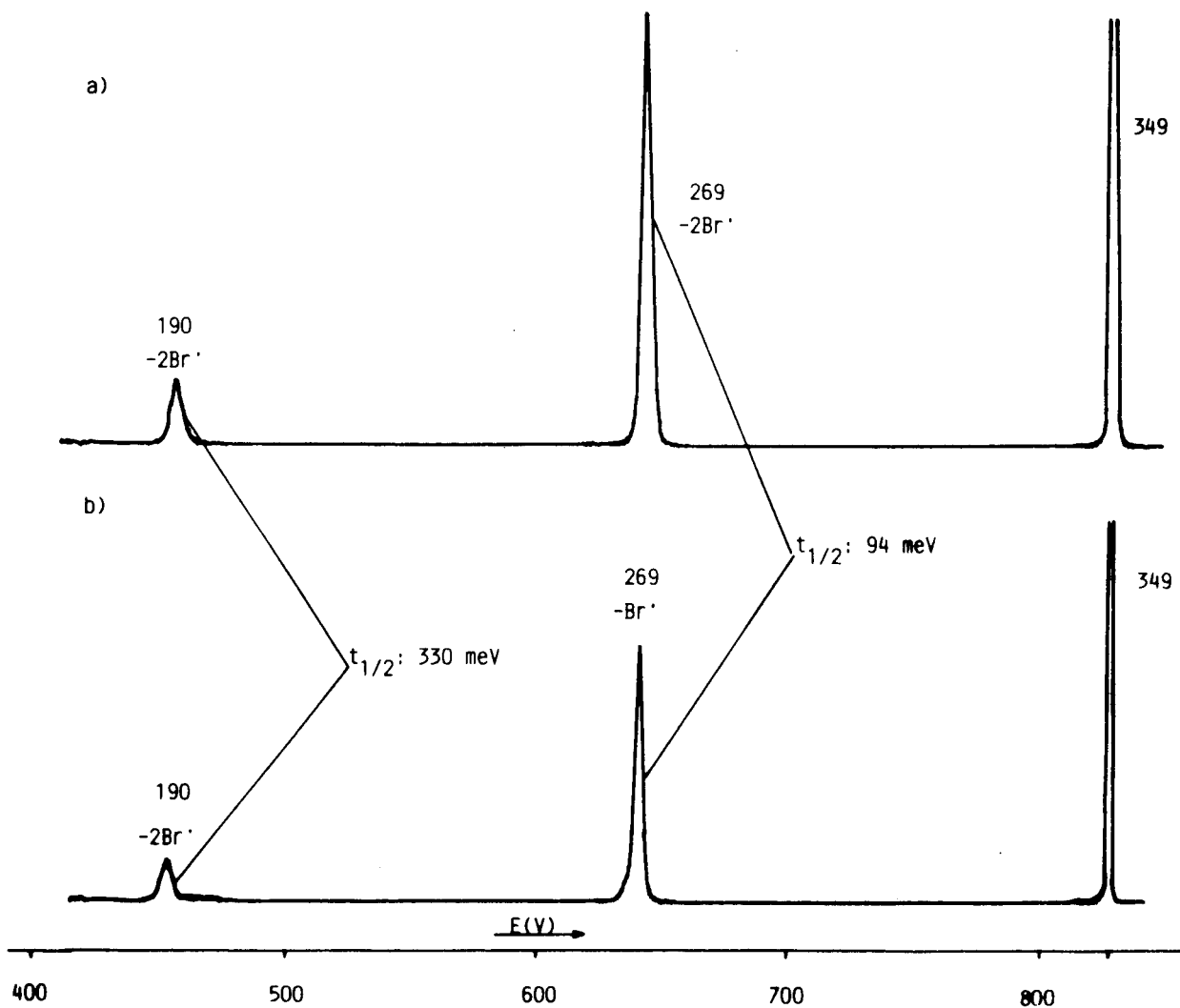


Figure 2. MIKE spectra of M^+ (m/z 348) for a) compound **2** and b) compound **3**.

Such cleavages showed a different kinetic process; in fact the absolute abundances of primary fragments at m/z 190 and 269 in the ion source and in the second free field region (II FFR), *i.e.* in two different time windows [6], demonstrated that the 2Br loss is the fastest process. In fact the $[M-2Br]^+/[M-Br]^+$ ratio increase from 0.16 to 15.5 passing from the II FFR to the ion source (as obtained by MIKE and EI spectra), for both **2** and **3** isomers. The same conclusion is obtained by the kinetic energy releases involved in the two fragmentations: values of 330 and 94 meV respectively for two and one Br loss was obtained for the both the isomers (Figure 2). These data emphasized the high stability of the fragment ions at m/z 190. The structure of these ions was confirmed by collisional spectroscopy [7] performed with 8 keV ions colliding with air in the II FFR at a pressure such as to reduce the main beam

intensity to 60% of its usual value. The ions at m/z 190 originated from **2** and **3**, showed collisional activated decomposition MIKE spectra superimposable with that obtained, in the same experimental conditions, from DTB synthesized *via* chemical cyclization (Figure 3). These data are in agreement with the above mentioned cyclization mechanism pictured in Scheme 3:

Scheme 3

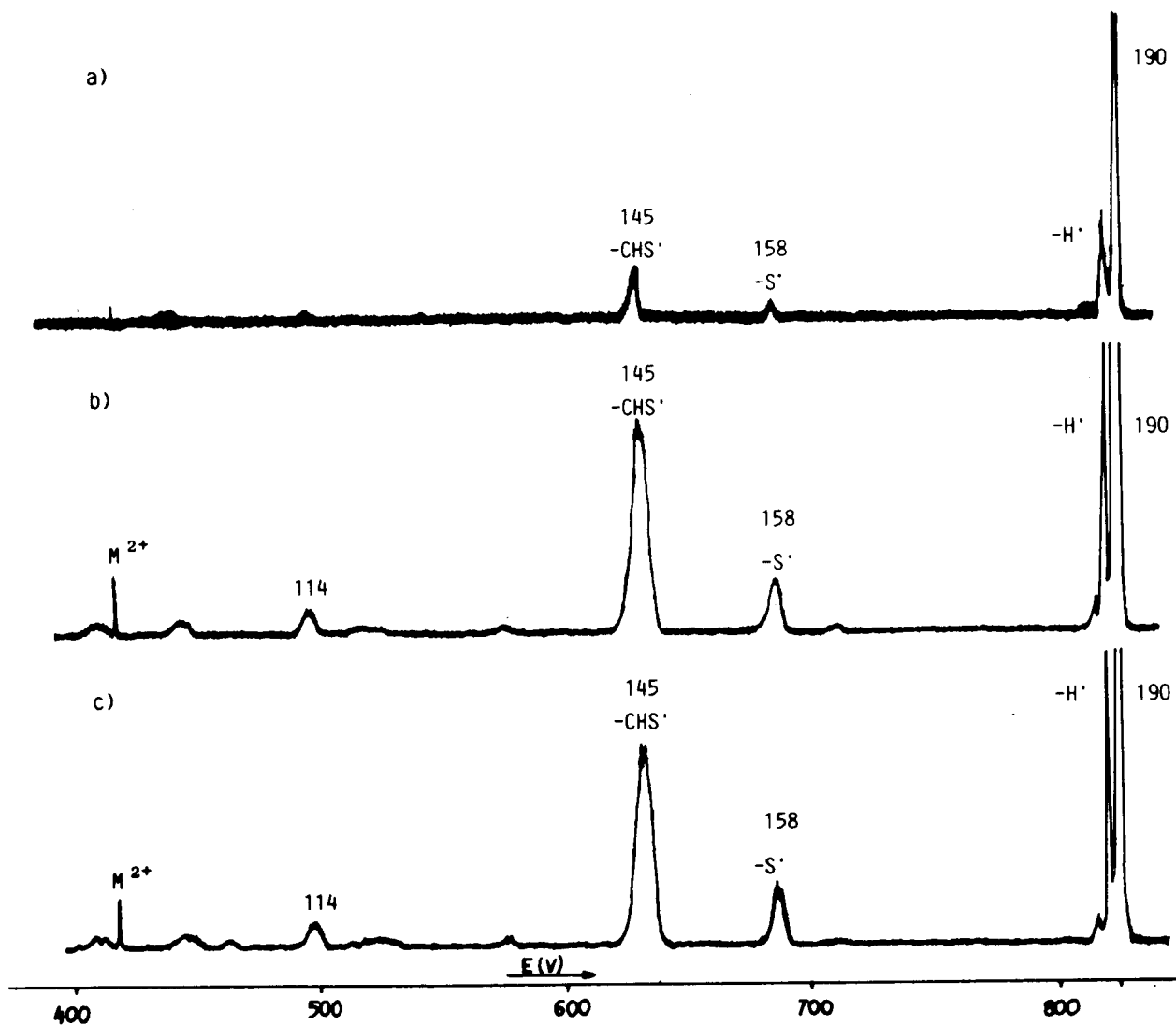
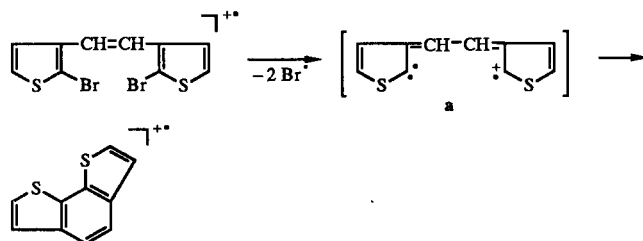


Figure 3. CAD-MIKE spectra of ionic species at m/z 190 corresponding to a) M^+ (m/z 190), b) $[M-2Br]^+$ from isomer **2** and c) $[M-2Br]^+$ from isomer **3**.

The loss of two bromine atoms produces a intermediate with high electron delocalization to which corresponds the loss of *cis* and *trans* configuration. The limit structure **a** evolves to cyclization product by means electron coupling. These results confirm that the energy involved in the mass spectrometric process is sufficient to abstract two bromine radicals.

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