

PHOTOCHROMISM OF SOME BRIDGED O-ANALOGUES OF  
THIATHIOPHTHENES

R. Gleiter, K.-H. Knauer and Erika Schmidt

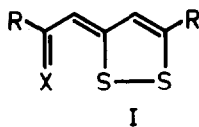
Physikalisch-Chemisches Institut der Universität Basel,  
4056 Basel (Switzerland)

Y. Mollier and R. Pinel

Laboratoire des Composés Thioorganiques Université de Caen, 14032 Caen  
Cedex (France)

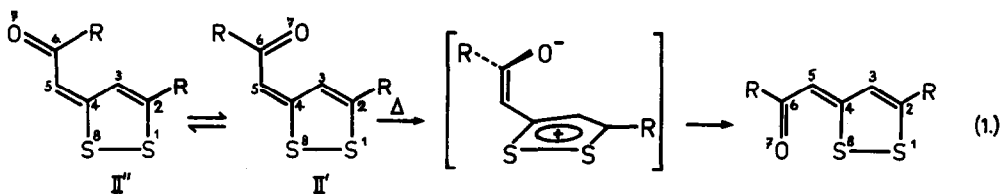
(Received in UK 12 February 1973; accepted for publication 2 March 1973)

Irradiation of dimethylthiathiophthene (Ia) as well as its N-phenylderivative (Ib) and its O-derivative (Ic) yields a photoproduct which reverts in a dark



|    | R                             | X                               | reaction to the starting                                  |
|----|-------------------------------|---------------------------------|---|
| Ia | CH <sub>3</sub>               | S                               | material [1]. The rates at 25 <sup>0</sup> C              |
| Ib | CH <sub>3</sub>               | N-C <sub>6</sub> H <sub>5</sub> | in ethanol are: k (Ia) = 616.6                            |
| Ic | CH <sub>3</sub>               | O                               | [sec <sup>-1</sup> ], k (Ib) = 204.2 [sec <sup>-1</sup> ] |
| Id | C <sub>6</sub> H <sub>5</sub> | O                               | and k (Ic) = 4.68 · 10 <sup>-3</sup> [sec <sup>-1</sup> ] |

Recently we were able to assign the structure of the photoproduct of Ic and Id to Iic and Iid by NMR- and IR-spectroscopy, while the kinetic results could be rationalized by assuming a polar transition state as shown in (1.) [1b,2]. In the structural assignment the question concerning the conformation of II with respect

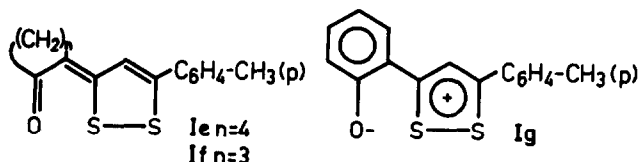


to a rotation around the bond C<sub>5</sub>-C<sub>6</sub> (II' or II'') was left open.

Here we report our studies of reaction (1.) for Ie and If. Both products

behave similarly to Ic and Id upon irradiation in a hydrocarbon solvent. A comparison of the photoproducts of Ic and Id with those of Ie and If should elucidate the problem of the conformation of II since in Ie and If only conformation II' is possible.

Additionally with Ig we are able to check the prediction [2] that an increase of the overlap population between the bond C<sub>5</sub>-C<sub>6</sub> should increase the rate of the thermal back reaction as compared with Ic - If. Our findings bearing on these



questions are as follows: The kinetics of the thermal back reaction for the photoproduct of Ig has been studied in toluene. The activation energy obtained from an Arrhenius plot was  $E_a = 8.94$  kcal/mol. Assuming the transition state theory we obtain  $\Delta G^*_{250} = 15.25$  kcal/mol and  $\Delta S^*_{250} = -23.17$  eu. The rates at 25°C in toluene were found to be:  $k$  (Ic) =  $5.89 \cdot 10^{-4}$  [sec<sup>-1</sup>],  $k$  (Id) =  $1.14 \cdot 10^{-3}$  [sec<sup>-1</sup>],  $k$  (If) =  $6.62 \cdot 10^{-5}$  [sec<sup>-1</sup>] and  $k$  (Ig) =  $41.22$  [sec<sup>-1</sup>] [3]. Indeed Ig reacts by a factor of  $10^4$ - $10^6$  faster than the other compounds.

In table 1, the  $\nu_{CO}$  wave numbers ( $C_2Cl_4$ ) of Ic-If are compared with those of IIC-IIf

Table 1

$\nu_{CO}$  wave numbers of Ic-If and IIC-IIf in  $C_2Cl_4$  (25°C)

| Compound                             | Ic      | IIC  | Id      | IId  | Ie      | IIE  | If   | IIf  |
|--------------------------------------|---------|------|---------|------|---------|------|------|------|
| $\nu_{CO}$ [cm <sup>-1</sup> ]       | 1595[5] | 1645 | 1559[5] | 1635 | 1569[4] | 1640 | 1634 | 1676 |
| $\Delta\nu_{CO}$ [cm <sup>-1</sup> ] | 50      |      | 76      |      | 71      |      | 38   |      |

The variation of  $\nu_{CO}$  for IIC-IIE is relatively small. This suggests that substituent effects play a minor role and that the relative large variation of  $\nu_{CO}$  for Ic-Ie is due to the partial bond between S and O. The S...O bond distances for Ic and Ie have been determined to be 2.41 Å [6] and 2.26 Å [7] respectively. If we use  $\Delta\nu_{CO}$  as indicative of the strength of the S...O partial bond in I, a S...O bond length over 2.4 Å is predicted for If, whereas Id should show a S...O distance similar to that of Ie.

In table 2, the NMR chemical shifts in  $C_2Cl_4$  at room temperature of the vinylic and dithiolic protons for Ic-If and IIC-IIf are compiled.

Table 2

NMR results for Ic-If and Iic-Iif in  $C_2Cl_4$  ( $25^\circ C$ ).  
(values in ppm with TMS as internal standard)

| Compound         | Ic   | Iic  | Id  | IId  | Ie   | Iie  | If  | IIf |
|------------------|------|------|-----|------|------|------|-----|-----|
| vinylic proton   | 6.56 | 6.02 | 7.4 | 6.9  | -    | -    | -   | -   |
| dithiolic proton | 6.75 | 8.21 | 7.6 | 9.07 | 7.38 | 8.98 | 7.0 | 8.7 |

To compare the results of Iic with those of IId-IIf we have to correct for the chemical shift induced by a phenyl substituent attached to the dithiole ring. A comparison of Ic with Id-If gives an estimate of 4-.5 ppm for the downfield shift. With this correction we obtain essentially the same chemical shift for all four samples suggesting that in each case conformation II' is favoured over conformation II". The observed downfield shift of the dithiolic proton in II [8] is due to the anisotropy of the carbonyl group (see also ref. [2]).

There is a small difference between the electronic spectra of Iic, IId and of Iie, IIf. While for Iic and IId the  $0 \rightarrow 0$  transition of the long wave length band is shifted bathochromically with respect to that of Ic or Id [2], this is not the case for Iie and IIf (see fig. 1).

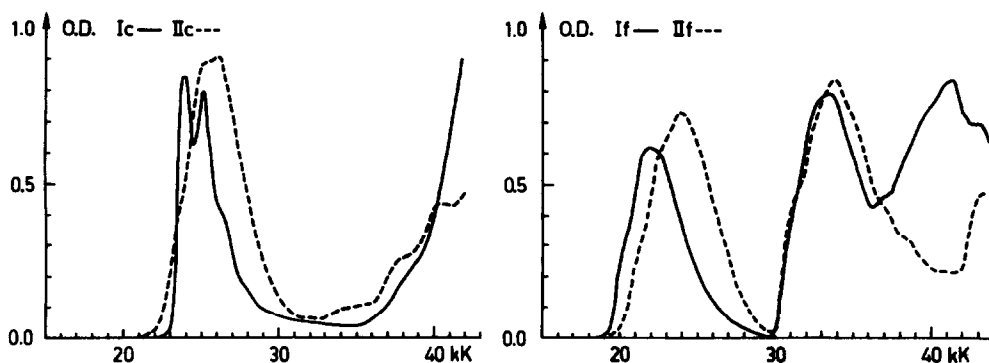


Fig. 1

Electronic spectra of Ic and Iic at  $-100^\circ C$  (left) and If and IIf at  $-50^\circ C$  (right). The spectra were recorded in 2,2'-dimethylbutane/n-pentane (8:3).

For IIf the thermal back reaction was too fast for the electronic spectrum to be recorded even at  $-140^\circ C$ . A qualitative spectrum however could be obtained with the flash technique. Isosbestic points are observed at 550, 420 and 340 nm. The long wavelength band in IIf shows a bathochromic shift with respect to the long

wavelength band in Ig.

The preparation of Ie and If has been described in ref. [9], that of Ig in ref. [10]. The technical details for obtaining the photoproducts are reported in ref. [2].

#### Acknowledgement

We thank Miss E. Rommel for measuring the electronic spectra and Dr. B. Kowert and PD Dr. P. Schiess for helpful comments. This work is part of project No. 2.477.71 of the Schweizerischer Nationalfonds. Financial support by CIBA-GEIGY SA, Basel, is gratefully acknowledged.

#### Footnotes and References

- [1] a) R. Gleiter, D. Werthemann and H. Behringer, *J. Amer. Chem. Soc.* **94**, 651 (1972); b) R. Gleiter, D. Werthemann and G. Calzaferri, paper No.2 presented at the First IUPAC Conference on Physical Organic Chemistry in Crans, Sept. 4-8, 1972.
- [2] G. Calzaferri, R. Gleiter, K.-H. Knauer, E. Rommel, E. Schmidt and H. Behringer, *Helv. Chim. Acta* in print.
- [3] For Ie reaction (1.) is not fully reversible, therefore k could not be determined.
- [4] R. Pinel and Y. Mollier, *Bull. Soc. chim. France*, **1972**, p. 1385.
- [5] D. Festal, O. Coulibaly, R. Pinel, C. Andrien and Y. Mollier, *Bull. Soc. chim. France*, **1970**, 2943, R. Pinel, dissertation Université de Caen, 1971.
- [6] M. Mammi, R. Bardi, G. Traverso and S. Bezzi, *Nature*, **192**, 1282 (1961).
- [7] R. Pinel, Y. Mollier, E.C. Llaguno and I.C. Paul, *Chem. Comm.*, **1971**, 1352.
- [8] The chemical shifts observed for the dithiolic protons in compounds II are quite similar to the one observed in 2-(5-phenyl-1,2-dithiole-3-ylidene)-5,5-dimethyl-1,3-cyclohexanedione,  $\delta = 9.71$  ppm ( $C_2Cl_4$ ), as reported by Y. Mollier, F. Terrier and N. Lozac'h, *Bull. Soc. chim. France*, **1964**, 1778.
- [9] O. Coulibaly and Y. Mollier, *Bull. Soc. chim. France*, **1969**, 3208
- [10] R. Pinel, Y. Mollier and N. Lozac'h, *Bull. Soc. chim. France*, **1967**, 856.