# Arylidene polymers: 11. Synthesis of poly[2,5-bis(*m*-nitrobenzylidene)-cyclopentanone sulphide] and some theoretical studies on its monomer unit

**Mohamed A. Abd-Alla* and Anwar S. El-Shahawy**
*Chemistry Department, Polymer Lab. 507, Faculty of Science, Assiut University, Assiut 71516, Egypt*
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Nitration of 2,5-bis(*p*-chlorobenzylidene)cyclopentanone (I) afforded the corresponding 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone (II). Polymerization of II with $Na_2S$ in *N*-methylpyrrolidone gave poly[2,5-bis(3-nitrobenzylidene)cyclopentanone sulphide]. The monomer was characterized by infra-red and $^1H$ nuclear magnetic resonance spectroscopy and elemental analysis. The polymer formed was confirmed by elemental analysis, infra-red spectroscopy, viscometry, differential thermal analysis measurements, thermogravimetry and X-ray analysis. An isothermal electrical conductivity test of the new polysulphide polymer indicates that it has a value of about $3.2 \times 10^{-3}$ ohm$^{-1}$ cm$^{-1}$ at 390 K. Using the Pariser–Parr–Pople method the C=O oxygen atom in compound II has a partially positive charge in the normal state, reduced and oxidized forms. The ionization potential and the electron affinity are not altered by replacing the sulphur atom, i.e. 9.55 (9.56) and 7.94 (7.77).

**(Keywords: synthesis; [2,5-bis-(*m*-nitrobenzylidene)cyclopentanone sulphide]; characterization; conducting polymer; calculation of properties)**

## INTRODUCTION

Conjugated organic polymers have gained increasing interest as electrically conducting polymers in recent years. Poly(*p*-phenylene)[1,2], poly(*p*-phenylene vinylene)[3,4], polypyrrole[5], polythiophene[6] and poly(phenylene sulphide)[7] have been of particular interest.

In previous work[8] we reported the synthesis of a new class of poly- and copoly-arylidenecycloalkanones as conjugated polymers that possess semiconducting properties upon doping with iodine. These polyarylidenes have attracted much attention because they are a new class of polymers and are expected to give highly conductive polymers.

The work reported here outlines the synthesis, characterization and electrical conductivity of poly[2,5-bis(*m*-nitrobenzylidene)cyclopentanone sulphide]. A major target of this work was to optimize the conditions for its preparation. The influence of monomer structure upon the polymer properties, such as thermal stability, solubility and crystallinity, was also studied. Furthermore, some theoretical studies using the Pariser–Parr–Pople (PPP) method were made for its monomer unit to define its chemical behaviour.

## EXPERIMENTAL

### *Materials*

2,5-Bis(*p*-chlorobenzylidene)cyclopentanone (I) was prepared as reported in previous work[8]. 4-Chloro-3-nitrobenzaldehyde and sodium sulphide-9$H_2O$ were purchased from Merck.

### *Measurements*

The elemental analysis was done on a Perkin–Elmer 240C instrument. The i.r. spectra were recorded on a Pye Unicam SP3 100 spectrophotometer using the KBr pellet technique. Proton n.m.r. spectra were run on a Varian EM 390 90 MHz n.m.r. spectrometer at room temperature in dimethylsulphoxide (DMSO) using tetramethylsilane (TMS) as internal reference. The inherent viscosity of a polymer solution of 0.5 g/100 ml in sulphuric acid was determined at 30°C using an Ubbelohde Suspended Level Viscometer. X-ray diffractograms were obtained with a Philips X-ray PW 1710 diffractometer, using Ni-filtered Cu $K_\alpha$ radiation. Thermogravimetric analysis and d.t.a. were carried out in air with Du Pont model 951, 910 and 1090 Thermal Analyzers at a heating rate of 10°C min$^{-1}$. Polymer samples in the form of discs with diameter 13 mm and thickness 1.2 mm were used for electrical conductivity measurements. These discs were made by using an i.r. die at a constant pressure of 1000 psi (6.895 MPa). Two standard graphite electrodes were contacted to the surface of the polymer sample and then mounted onto a temperature-controlled electric furnace provided with a standard copper/constantan thermocouple. Conductivity was measured over the temperature range of 300–400 K using a Keithley 610C Electrometer. Iodine doping was accomplished by a vapour-phase technique[9].

* To whom correspondence should be addressed

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*Monomer synthesis*

2, 5-Bis(4-chloro-3-nitrobenzylidene)cyclopentanone (II) was prepared by nitration of 2,5-bis(4-chlorobenzylidene)cyclopentanone in poor yield (30%). It was also prepared by condensation of 2 mol of 4-chloro-3-nitrobenzaldehyde with 1 mol of cyclopentanone as described before[8] in quantitative yield (90%) and crystallized from acetic acid; m.p. 253°C. I.r. (KBr) showed bands at 1680 $cm^{-1}$ (C=O stretching of cyclopentanone), 1600 $cm^{-1}$ (C=C stretching), 1560, 1330 $cm^{-1}$ (C–$NO_2$) and 800 $cm^{-1}$ (C–Cl stretching vibration). $^1H$ n.m.r. (DMSO), $\delta$ = 7.6 ppm (m, 2H of 2 CH=C), 7.10–7.5 ppm (m, 6H of Ar–H) and 3.3 ppm (4H of 2 $CH_2$ cyclopentanone).

*Synthesis of polymer*

The polymer was synthesized by a similar method[10] to that in a patent issued to Edmunds and Hill of Philips Petroleum on the synthesis of arylene sulphide polymers.

In a reaction flask, 6 g of sodium sulphide-9$H_2O$ in 100 ml of *N*-methylpyrrolidone (NMP) was heated to 160°C while flushing with nitrogen. Then 10.3 g of 2,5-bis(4-chloro-3-nitrobenzylidene)cyclopentanone (II) was added and the dispersion heated in a temperature-controlled electric furnace for 24 h at 290°C. At the end of this time the reaction mixture was cooled to room temperature and then poured onto ice-cold water, where a deep brown fine powder was isolated. It was filtered off, washed with water, ethanol and acetone, and dried at 80°C in vacuum at 0.1 mmHg for 2 days.

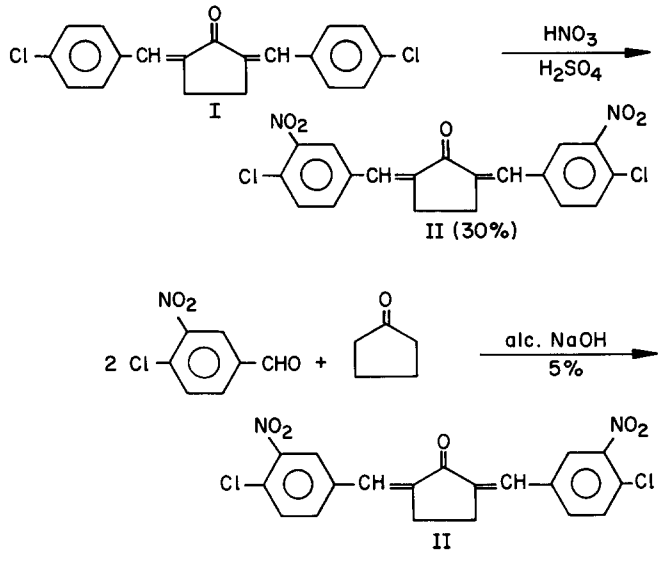
Analysis calculated for $C_{19}H_{12}O_5H_2S$: C 60.00, H 3.17, N 7.37, S 8.42; found: C 60.11, H 3.25, N 7.12, S 8.52.

## RESULTS AND DISCUSSION

The preparation of poly[2,5-bis(*m*-nitrobenzylidene)-cyclopentanone sulphide] was based upon the synthesis of 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone (II) as a monomer for the polymerization process. This precursor was synthesized by two routes. In the first one a direct nitration reaction[11] for 2,5-bis(*p*-chlorobenzylidene)cyclopentanone (I) was used to obtain the corresponding 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone (II). It was found that using this method afforded a poor yield (30%) of the desired monomer. Because of the disadvantages of the nitrate pathway, the monomer was prepared via facile condensation of 2 mol of *p*-chloro-*m*-nitrobenzaldehyde with 1 mol of cyclopentanone in quantitative yield (90%) as described in previous work[8]. All the methods used for the synthesis are depicted in *Scheme 1*.

The monomer was polymerized in the presence and absence of solvent. Mass polymerization in the absence of solvent was carried out, and it was found that instantaneous and uncontrolled reactions generally occurred, producing infusible and insoluble resin. Therefore, the monomer was polymerized by a solution polymerization technique and in the presence of NMP as reported previously in a patent[10] on the synthesis of poly(*p*-phenylene sulphide).

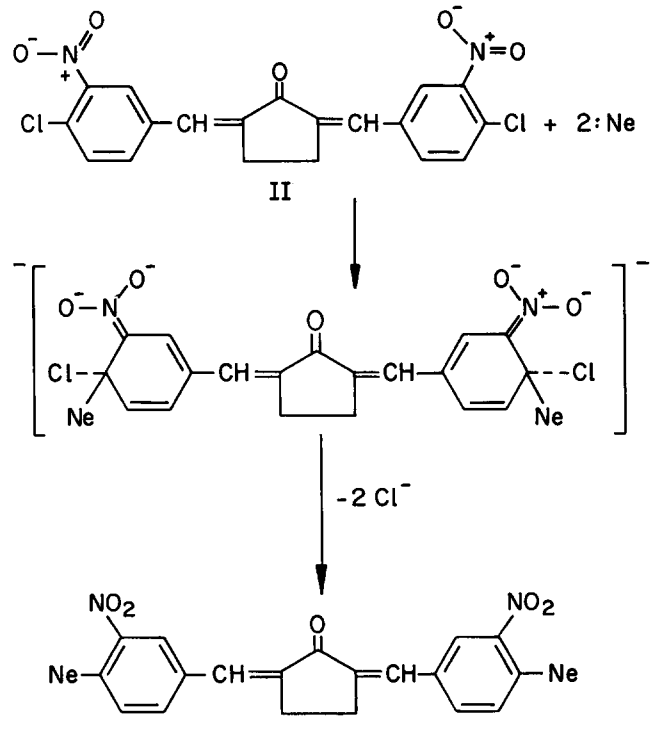
The basic reaction of the polymerization is an aromatic nucleophilic substitution. At present, there are two fairly well defined mechanisms[12] for the substitution of aryl halide by nucleophilic substituent. The two mechanisms are (i) the addition–elimination reaction of aryl halides,



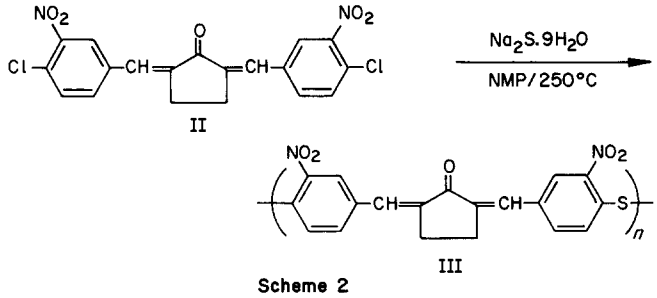

**Scheme I**

generally activated by resonance interaction with a powerful electron-withdrawing group, or (ii) the elimination–addition reaction of unactivated aryl halides catalysed by strong base, often referred to as the aryne mechanism.

In the present work the addition–elimination nucleophilic reaction mechanism is pronounced and the displacement of $Cl^-$ from 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone involves the formation of an intermediate anion as shown in the following equation (where Ne is a nuclephilic substituent):




Therefore, 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone was easily polymerized with sodium sulphide-9$H_2O$ in the presence of NMP and afforded the corresponding polysulphide polymer in good yield as shown in *Scheme 2*.




Scheme 2

The new synthesized polysulphide (III) was characterized by elemental analysis, i.r. spectral data, viscometry measurements, t.g.a., d.t.a. and X-ray analyses. Moreover, the electrical conductivity of the new polysulphide (III) was also measured over the temperature range of 300 to 400 K.

The elemental analysis of polymer III coincided with its characteristic repeat unit, which reveals the introduction of a new sulphur atom into it. The i.r. spectrum of the resulting polymer shows characteristic absorption bands at 1685 $cm^{-1}$ (s, C=O of cyclopentanone), 1595 $cm^{-1}$ (m, C=C stretching) and 1540 $cm^{-1}$ (s, C–$NO_2$ group). In addition, other characteristic absorption bands, due to specific groups present in the rest of the macromolecule, are seen.

The solubility characteristics of polymer III were tested in various solvents, including NMP, dimethylacetamide (DMA), dimethylformamide (DMF), $CH_2Cl_2$, *m*-cresol, phenol, tetrachloroethene, conc. $H_2SO_4$, methanesulphonic acid, dichloroacetic acid and chlorosulphonic acid. It was found that the polymer is partially soluble in aprotic solvents such as NMP, DMA and DMF, and swells without dissolving in halogenated solvents. In protic solvents such as conc. $H_2SO_4$ and chlorosulphonic acid the polymer dissolved readily, and a deep violet or dark blue solution was obtained.

The inherent viscosity of a polymer solution (0.5% w/v) in conc. $H_2SO_4$ was determined at 30°C using an Ubbelohde Suspended Level Viscometer and gave the value of 0.52 dl $g^{-1}$.

The thermal behaviour of polymer III was evaluated by t.g.a. and d.t.a. in air at a heating rate of 10°C $min^{-1}$. The t.g. curve of polymer III in *Figure 1* shows a small weight loss in the range of 2.3% above 150°C, and this may be attributed to loss of adsorbed moisture and entrapped solvents. More particularly, the temperature at which 5% weight loss occurs is considered to be the polymer decomposition temperature. Therefore, the thermogram indicates that the polymer starts to decompose at 440°C, and above this temperature a fast decomposition is observed.

The X-ray diffractogram of polymer III in *Figure 2* shows a few reflections of sharp peaks intermediate between crystalline and amorphous interferences in the region of $2\theta$ = 5–45°C. This indicates that there is a large class of structures in the polymer main chain in the ordered state.

## THEORETICAL STUDIES

From the Pariser–Parr–Pople (self-consistent field)–configuration interaction (PPP(SCF)–CI) calculation[13–15] of 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone, it has been concluded tha the $\pi$-electronic energy of the planar *trans* form is lower than that of the planar *cis* form in the ground state by the value 5.626 eV (*Figure 3*).

Dealing with the SCF charge densities, the negative charges are concentrated on the nitrogen oxygen atoms, but the cyclopentanone moiety has higher values of the positive charge. The carbonyl oxygen atom has a partial positive charge as a result of the presence of the nitro groups, in contrast to the reported normal carbonyl oxygen atom in dibenzylidenecyclopentanone[15]. An elimination or an addition of an electron, e.g. through electrolysis, does not alter its partial positive charge (see *Table 1*).

From *Tables 2* and *3*, it has been found that the chlorine atom has a considerable contribution in the lowest unoccupied molecular orbital (LUMO) in comparison with its highest occupied molecular orbital (HOMO) contribution. Hence it is affected by a reduction process, which can be realized by nucleophilic attack. In this case the bond order is minimized between the chlorine atom and the benzene nucleus. This means that the nucleophilic substitution reaction occurs.

From a general point of view, the SCF HOMO is mainly spread over the nitro groups, while the SCF LUMO is localized over the 2-oxo-1,3-cyclopentanediylidenyl moiety.

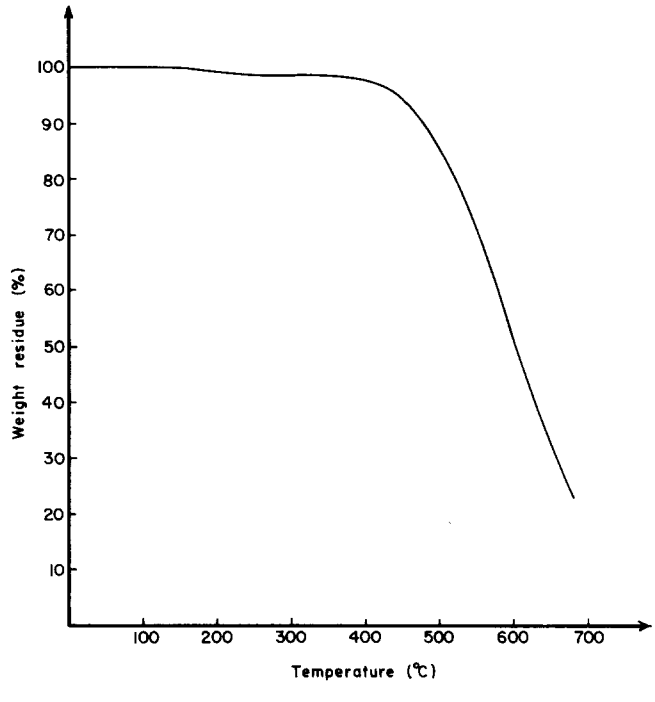



**Figure 1** Thermogravimetric curve of polymer III

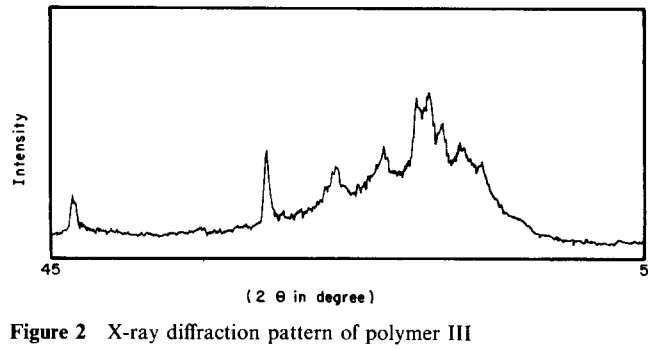



**Figure 2** X-ray diffraction pattern of polymer III

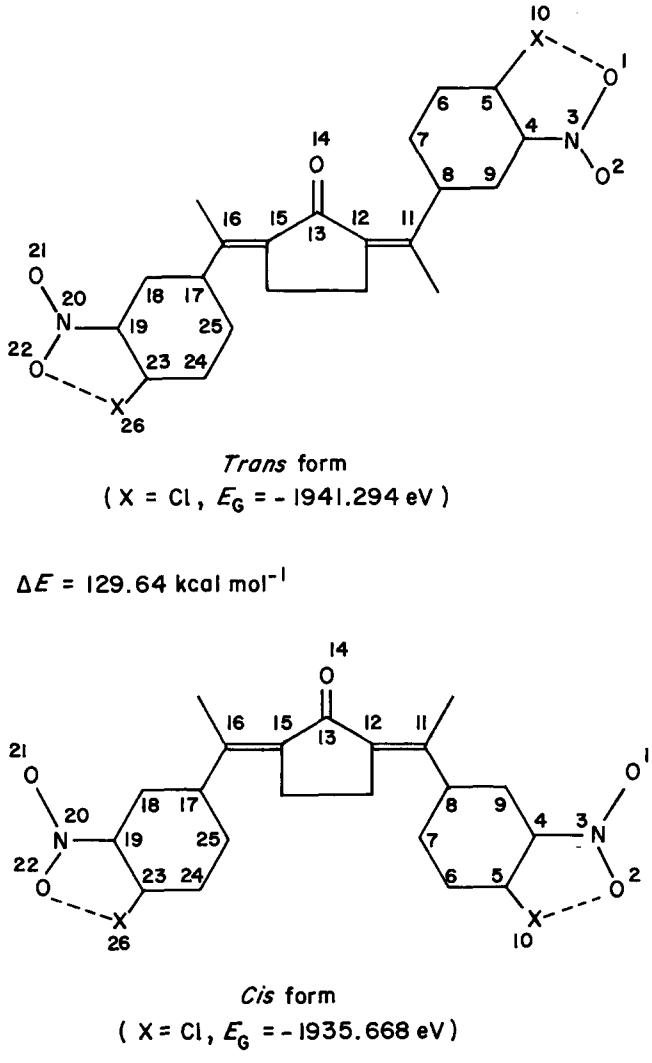



**Figure 3** The possible structures of the studied monomers (X = Cl, SH)

**Table 1** The charge densities of 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)-cyclopentanone in the three states

| Atom | Molecule | Cation | Anion |
|---|---|---|---|
| 1(21) | −0.9925 | −0.8212 | −0.9942 |
| 2(22) | −0.9925 | −0.8212 | −0.9942 |
| 3(20) | +0.0339 | +0.1339 | +0.0310 |
| 4(19) | +0.0783 | +0.1073 | +0.0623 |
| 5(23) | +0.4179 | +0.4220 | +0.3046 |
| 6(24) | +0.0138 | +0.0227 | +0.0100 |
| 7(25) | +0.2607 | +0.2764 | +0.1910 |
| 8(17) | +0.2665 | +0.2665 | +0.1928 |
| 9(18) | +0.0961 | +0.1510 | +0.0679 |
| 10(26) | +0.0002 | +0.0002 | +0.0001 |
| 11(16) | +0.1796 | +0.1898 | +0.1418 |
| 12(15) | +0.5202 | +0.5279 | +0.3724 |
| 13 | +0.1323 | +0.1333 | +0.1323 |
| 14 | +0.1018 | +0.1156 | +0.1018 |

In the case of the corresponding theoretical thio monomer model 2,5-bis(*p*-mercapto-*m*-nitrobenzylidene)-cyclopentanone (*Tables 4* and *5*), the carbonyl oxygen atom has a partial positive charge in the normal state as well as in the oxidized form as a cation, but it has a partial negative charge in the reduced form as an anion. On the other hand, the introduction of the sulphur atom instead of the chlorine atom increases its contribution in the HOMO as well as in the LUMO (*Table 3*); therefore the sulphur atom can be affected by oxidation or reduction processes.

The ionization potential and the electron affinity were calculated according to Pople[16]:

$$E = \sum_u \sum_v C_{mu} C_{mv} F_{uv}$$

From the values of the ionization potentials and the electron affinities, it is obvious that the introduction of the sulphur atom instead of the chlorine atom does not strongly alter their values (*Table 6*).

The electrical conductivity of the newly synthesized polysulphide III was measured according to the Arrhenius relation at room temperature, 300 K. The results show that the virgin sample of the polysulphide III possesses an electrical conductivity value of about $2.3 \times 10^{-12}$ ohm$^{-1}$ cm$^{-1}$. This reflects the onset of semiconductor behaviour.

Preliminary thermal studies for the polymer over the temperature range 300–400 K show that the conductivity behaviour follows a one-term Arrhenius-type equation (straight line) and the conductivity increases with increasing temperature and has a value of about $3.2 \times 10^{-3}$ ohm$^{-1}$ cm$^{-1}$ at 390 K. From the charge density point of view (cf. *Table 4*), it shows that the theoretical thio monomer model has negative poles in the edges and a positive hole in the 2-oxo-1,3-cyclopentanediylidene

**Table 2** The SCF bond orders of 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone in the three states

| Bonded atoms | | Molecule | Cation | Anion |
|---|---|---|---|---|
| 1(21) | 3(20) | 0.01365 | 0.14450 | 0.01142 |
| 2(22) | 3(20) | 0.01365 | 0.14450 | 0.01142 |
| 3(20) | 4(19) | 0.17780 | 0.23161 | 0.17092 |
| 4(19) | 5(23) | 0.43946 | 0.42866 | 0.48205 |
| 5(23) | 6(24) | 0.56854 | 0.57452 | 0.58915 |
| 6(24) | 7(25) | 0.78118 | 0.76939 | 0.76501 |
| 7(25) | 8(17) | 0.28725 | 0.28741 | 0.35900 |
| 8(17) | 9(18) | 0.39464 | 0.39435 | 0.44021 |
| 9(18) | 4(19) | 0.80784 | 0.76795 | 0.78662 |
| 10(26) | 5(23) | 0.01622 | 0.01629 | 0.01446 |
| 11(16) | 8(17) | 0.69128 | 0.69141 | 0.63844 |
| 12(15) | 11(16) | 0.54293 | 0.53410 | 0.61773 |
| 13 | 12(15) | 0.34598 | 0.34886 | 0.34599 |
| 14 | 13 | 0.84621 | 0.84236 | 0.84621 |

**Table 3** The SCF HOMOs ($\psi_m$) and the SCF LUMOs ($\psi_{m+1}$) of 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone (II) and 2,5-bis(*p*-mercapto-*m*-nitrobenzylidene)cyclopentanone

| | Compound II | | Theoretical model | |
|---|---|---|---|---|
| Atom | $\psi_m$ | $\psi_{m+1}$ | $\psi_m$ | $\psi_{m+1}$ |
| 1(21) | 0.41391 | 0.04100 | 0.41727 | 0.04180 |
| 2(22) | 0.41391 | 0.04100 | 0.41727 | 0.04180 |
| 3(20) | −0.31612 | −0.05438 | −0.31710 | −0.05780 |
| 4(19) | 0.17022 | 0.12651 | 0.16402 | 0.14140 |
| 5(23) | 0.06345 | 0.33662 | 0.05794 | 0.32425 |
| 6(24) | −0.09419 | 0.06121 | −0.08252 | 0.08750 |
| 7(25) | −0.12514 | −0.26408 | −0.10623 | −0.22363 |
| 8(17) | −0.00126 | −0.27159 | 0.00822 | −0.27757 |
| 9(18) | 0.23432 | −0.16777 | 0.23424 | −0.14618 |
| 10(26) | −0.00114 | −0.00524 | −0.01988 | −0.08948 |
| 11(16) | −0.10083 | 0.19456 | −0.10770 | 0.15490 |
| 12(15) | −0.08764 | 0.38442 | −0.09758 | 0.35022 |
| 13 | 0.03276 | 0.00000 | 0.03562 | −0.00559 |
| 14 | 0.11753 | −0.00104 | 0.12820 | −0.39751 |

**Table 4** The charge densities of 2,5-bis(*p*-mercapto-*m*-nitrobenzylidene)cyclopentanone as theoretical model

| Atom | Molecule | Cation | Anion |
|---|---|---|---|
| 1(21) | −0.9915 | −0.8174 | −0.9932 |
| 2(22) | −0.9915 | −0.8174 | −0.9932 |
| 3(20) | +0.0364 | +0.1370 | +0.0331 |
| 4(19) | +0.0870 | +0.1139 | +0.0670 |
| 5(23) | +0.4753 | +0.4787 | +0.3702 |
| 6(24) | +0.0166 | +0.0234 | +0.0089 |
| 7(25) | +0.2168 | +0.2281 | +0.1668 |
| 8(17) | +0.2958 | +0.2959 | +0.2188 |
| 9(18) | +0.0839 | +0.1388 | +0.0626 |
| 10(26) | +0.0598 | +0.0602 | +0.0518 |
| 11(16) | +0.1396 | +0.1511 | +0.1156 |
| 12(15) | +0.4731 | +0.4826 | +0.3504 |
| 13 | +0.1328 | +0.1341 | +0.1328 |
| 14 | +0.0633 | +0.0797 | −0.0946 |

**Table 5** The SCF bond orders of 2,5-bis(*p*-mercapto-*m*-nitrobenzylidene)cyclopentanone

| Bonded atoms | | Molecule | Cation | Anion |
|---|---|---|---|---|
| 1(21) | 3(20) | 0.01529 | 0.14761 | 0.01288 |
| 2(22) | 3(20) | 0.01529 | 0.14761 | 0.01288 |
| 3(20) | 4(19) | 0.18372 | 0.23570 | 0.17555 |
| 4(19) | 5(23) | 0.39859 | 0.38909 | 0.44444 |
| 5(23) | 6(24) | 0.50232 | 0.50710 | 0.53069 |
| 6(24) | 7(25) | 0.82034 | 0.81157 | 0.80077 |
| 7(25) | 8(17) | 0.28365 | 0.28452 | 0.34572 |
| 8(17) | 9(18) | 0.39099 | 0.38906 | 0.43156 |
| 9(18) | 4(19) | 0.82162 | 0.78320 | 0.80095 |
| 10(26) | 5(23) | 0.28426 | 0.28541 | 0.25524 |
| 11(16) | 8(17) | 0.67329 | 0.67417 | 0.63029 |
| 12(15) | 11(16) | 0.59476 | 0.58425 | 0.64901 |
| 13 | 12(15) | 0.33328 | 0.33675 | 0.33524 |
| 14 | 13 | 0.85836 | 0.85379 | 0.85613 |

**Table 6** The ionization potentials ($E_m$) and electron affinities ($E_{m+1}$) of the studied molecule

| Compound | $E_m$ (eV) | $E_{m+1}$ (eV) |
|---|---|---|
| I (X = Cl) | 9.55 | 7.94 |
| II (X = SH) | 9.56 | 7.77 |

moiety. This means that this molecule contains an intramolecular charge transfer in which the nitro groups act as an acceptor and the 2-oxo-1,3-cyclopentanediylidene moiety acts as a donor, owing to the pronounced conjugation of the mer. Hence, conjugation is responsible for the conductivity mechanism and is extended over the macrostructure of the polymer across the lone pair of electrons of the sulphur atom. Experimentally, doping with $I_2$ does not significantly alter the electrical conductivity of the polymer. Moreover, theoretical studies by PPP(SCF) reveal that the charge distribution features of the cationic form of the theoretical model of the repeat unit of the polysulphide (*Table 4*) are not significantly changed by elimination of an electron by an acceptor such as $I_2$ (doping agent).

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