

## Cresols—An Investigation into Their Electronic Structure and Spectra

K. P. Krishnan Namboodiri<sup>a</sup>, S. Viswanathan<sup>a</sup>,  
R. Ganesan<sup>a</sup>, and V. C. Jyothi Bhasu<sup>b, \*</sup>

<sup>a</sup> Department of Physical Chemistry, University of Madras,  
Madras-600 025, India

<sup>b</sup> Department of Inorganic and Physical Chemistry,  
Indian Institute of Science, Bangalore-12, India

(Received 24 August 1981. Accepted 5 November 1981)

The three isomeric cresols were subjected to the all-valence-electron CNDO/2 and PPP-CI calculations. Results from this study were used:

- (i) to compare the electronic structures of these isomers vis-à-vis parent compounds—phenol and toluene,
- (ii) to obtain a quantitative picture of their chemical reactivities and electronic absorption spectra.

Using the  $\sigma$ -core charges derived from CNDO/2 calculations and subsequently revising the valence-state ionisation potential and one-center-two-electron repulsion integrals, the PPP-CI calculations were performed on the title compounds according to *Nishimoto* and *Forster* scheme. In these calculations the pseudo-unsaturated nature of the methyl group has been given due consideration. In spectral assignment, compared to the conventional PPP approach, the CNDO/2-based PPP-CI method gave a better agreement with the experimental data.

(Keywords: Computation, CDNO/2 based-PPP-CI, Cresols)

### *Eine Untersuchung der elektronischen Struktur und der Spektren von Kresolen*

Drei isomere Kresole wurden mittels CNDO/2- und PPP-CI-Methoden untersucht; die Ergebnisse wurden bei den folgenden Untersuchungen benutzt:

- (i) Vergleich der elektronischen Strukturen dieser Verbindungen in bezug auf die Stammverbindungen Phenol und Toluol,
- (ii) eine quantitative Aussage über ihre chemischen Reaktivitäten und die Absorptionsspektren.

---

\* Present address: Donnan Laboratories, University of Liverpool, Grove Street, L69 3BX, England.

Mit Hilfe von CNDO/2 abgeleiteten  $\sigma$ -Ladungswerten, dem daraus ermittelten Valenz-Ionisations-Potential und Ein-Zentrum-zwei-Elektronen-Integralen wurden die PPP-CI-Berechnungen nach dem Schema von *Nishimoto* und *Forster* ausgeführt. Die pseudo-ungesättigte Rolle der Methylgruppe wurde berücksichtigt. Im Gegensatz zur PPP-Näherung zeigte die auf CNDO/2 bezogene PPP-CI-Methode bei den Berechnungen der Spektren eine bessere Übereinstimmung mit den experimentellen Daten.

### Introduction

In recent times, semiempirical computations on the electronic structure of molecules have attained considerable importance. The method involves theoretical calculations, using sophisticated computer programs, in order to explain and predict the effect of substituents on various physical characteristics and reactivities of organic molecules<sup>1,2</sup>. A brief survey of the literature indicates that a lot of theoretical work<sup>3-7</sup> has been carried out on the electronic structure of monosubstituted benzenes containing either electron-donating ( $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{CH}_3$ ) or electron-withdrawing ( $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{COOH}$ ) groups but much less attention has been paid to disubstituted benzenes where both the substituents are electron donating. In this context cresols form a very interesting class of compounds with their wide industrial applications in colour photography, synthetic dyes and polymers. The present paper deals with the results of complete neglect of differential overlap (CNDO/2), CNDO/2-based-*Pariser-Parr-Pople* (PPP)-CI and conventional PPP calculations on the three isomeric cresols.

Among the cresol isomers, *ortho*-cresol has attracted much attention due to its controversial conformations<sup>8-10</sup>. Very reliable quantum mechanical tools like *ab initio* and CNDO/2 methods have been applied to *ortho*-cresol. Although a lot of plausible results were obtained, unambiguous conclusions could not be arrived at<sup>8</sup>. *Allinger* and co-workers<sup>9</sup> predicted, based on molecular mechanics and dipole-moment measurements, the *trans*-orientation of the hydroxyl hydrogen with the methyl group to be the stable conformation for *ortho*-cresol. According to these authors<sup>9</sup> any weak hydrogen-bonding between the  $-\text{OH}$  and  $-\text{CH}_3$  groups has been ruled out and the repulsive interaction of the methyl group with the hydroxyl hydrogen has been given more importance. However, recently *Kudchadker* and others<sup>10</sup>, from potential energy (based on CNDO/2 calculations) and entropy parameters, inferred that the more stable conformation is the *cis*-orientation of the hydroxyl hydrogen to the methyl group and predicted the existence of two less stable *trans*-conformed species with almost equal probability.

*Meta*- and *para*-cresols have not received any attention in this type of study. Therefore a systematic investigation of the three isomers seems to be worth undertaking, with the aim of comparing their electronic structure and

reactivity in the light of quantum chemical calculations. The dependability of the all-valence-electron CNDO/2 and similar methods for electronic structure and reactivity correlations has been well established<sup>11-13</sup>.

Although the electronic absorption spectra of cresols have been reported by various authors<sup>14-17</sup> no serious attempt seems to have been made towards a quantitative interpretation of the electronic spectra based on theoretical calculations. The SCF LCAO-MO-*PPP* method is well known in explaining the  $\Pi$ -electronic absorption spectra of aromatic systems<sup>7, 18, 19</sup>. However, its limitations when applied to substituted benzenes containing substituents like the nitro-group, have been pointed out<sup>6</sup>.

In the present work, we use a modified *PPP* method wherein the  $\sigma$ -core charges are defined by foregoing CNDO/2 calculations along with other suitably modified parameters. The results of this modified *PPP* studies on a few systems have been reported elsewhere<sup>6, 20, 21</sup> and were found to be encouraging. The well known hyper-conjugative effect of the methyl group is an important factor in cresols and it was attempted earlier<sup>22</sup> to include this effect into the *PPP* scheme. The hyper-conjugative effect of methyl group has been taken into account in the present study by considering the methyl group as a "pseudo-unsaturated moiety"<sup>23</sup>.

### Method of Calculation

Conventional *PPP* schemes invariably use integral  $\sigma$ -core charges, for example, in phenol, +1 for carbon and +2 for oxygen. This procedure has been found to be satisfactory in the case of simple aromatics<sup>18, 19</sup>. But, in disubstituted benzene derivatives like dinitrobenzenes the *PPP* scheme gave erroneous results<sup>24</sup>. *Gordon* and *Neumer*<sup>6</sup> attributed this discrepancy to the use of integral  $\sigma$ -core charges. A more realistic picture of the molecule would obviously involve fractional  $\sigma$ -core charges which can be obtained by performing *a priori* all-valence-electron calculation of the molecule under consideration. In the present study we have carried out the CNDO/2 calculation for all the three isomeric cresols and the  $\sigma$ -core charges thus obtained are used in the *PPP* scheme. The improvement in the result will be evident when the conventional *PPP* and modified *PPP* methods are compared (Table 5).

For CNDO/2 calculations the standard program available<sup>25</sup> was used and for the *PPP*-CI scheme a program written by the authors in Fortran IV was employed. The present *PPP*-CI procedure is similar to the *Nishimoto* and *Forster*<sup>26</sup> parameter scheme which has been found to be capable of reproducing very well both the spectral maxima and the relative intensities of mono- and poly-substituted benzenes. For the

two-electron two-center repulsion integral, we have used the formula suggested by *Nishimoto* and *Mataga*<sup>27</sup>. The  $\beta$ -resonance integrals were transferred from similar molecules<sup>28</sup> and then modified after taking into account the  $\Pi$ -bond orders available from our CNDO/2 calculations.

Table 1. Summary of  $\Pi$ -electron parameters for cresols

Atom ( $\sigma$ -core charge)	Valence state ionisation energy eV	One-centre repulsion integral $\gamma_{\mu\mu}$ , eV
H (1.00)	— 8.50	8.50
C (0.96)	— 10.66	10.91
C (0.97)	— 10.79	10.97
C (1.00)	— 11.16	11.13
C (1.01)	— 11.28	11.19
C (1.02)	— 11.41	11.24
C (1.03)	— 11.53	11.30
C (1.12)	— 12.65	11.79
C (1.14)	— 12.90	11.90
O (1.70)	— 28.34	19.64

$\beta$ Resonance integrals, eV	
$\beta_{\text{C-OH}} = -1.80$	$\beta_{\text{C-CH}_3} = -1.60$
$\beta_{\text{C-C}} = -2.386$	$\beta_{\text{C}\equiv\text{H}_3} = -3.0$

The valence state ionisation potential and two-electron-one-center repulsion integrals for different atoms of non-integer  $\sigma$ -core charges were derived by linear interpolation of the corresponding +1 and +2 parameters given by *Nishimoto* and *Forster*. The  $\Pi$ -electron parameters for the carbon atoms were derived similarly by using the  $\text{C}^{2+}$  values reported by *Dewar* and *Morita*<sup>29</sup>. The parameters for methyl hydrogen and carbon were taken from already available data<sup>28, 30</sup>. The methyl group has been considered as a  $-\text{C}\equiv\text{H}$  moiety accounting for its hyper-conjugative effect in *PPP*-CI calculation. A summary of the  $\Pi$ -electronic parameters used are presented in Table 1. The geometries for these molecules in the present calculations were taken from the recent structure reports and represented with modifications in Fig. 2. All the calculations were performed on a DEC-1090 computer system.

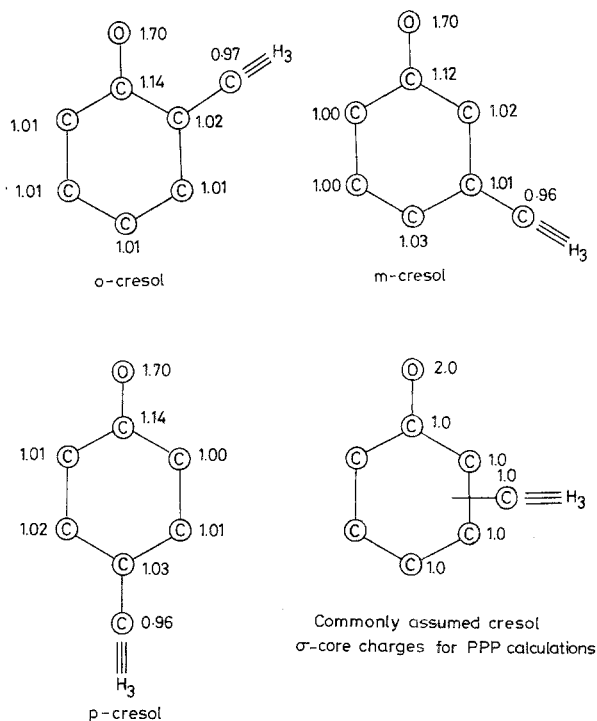


Fig. 1. Proposed  $\sigma$ -core charges for isomeric cresols based on CNDO/2 calculations

## Experimental

All the three isomeric cresols (AnalaR BDH) were used after redistillation. The solvent methanol was purified<sup>31</sup>, distilled under vacuum and then used. All the solutions were prepared carefully and protected by black cloth to avoid any photochemical reaction. The electronic spectra of the cresols were recorded in a Beckmann (model 25) UV-Visible spectrophotometer in the range 350 to 200 nm at 25 °C.

## Results and Discussion

### *Electronic Structure*

The electron density distribution (both  $\Pi$  and  $\sigma$ ) for the three cresols and phenol is given in Table 2. The numbering convention and geometry used in CNDO/2 and PPP-CI calculations are shown in Fig. 2. It is interesting to note that the results of net-charges and  $\Pi$  bond-orders obtained from both the CNDO/2 and PPP-CI (modified) are in fair agreement (Tables 3 and 4).

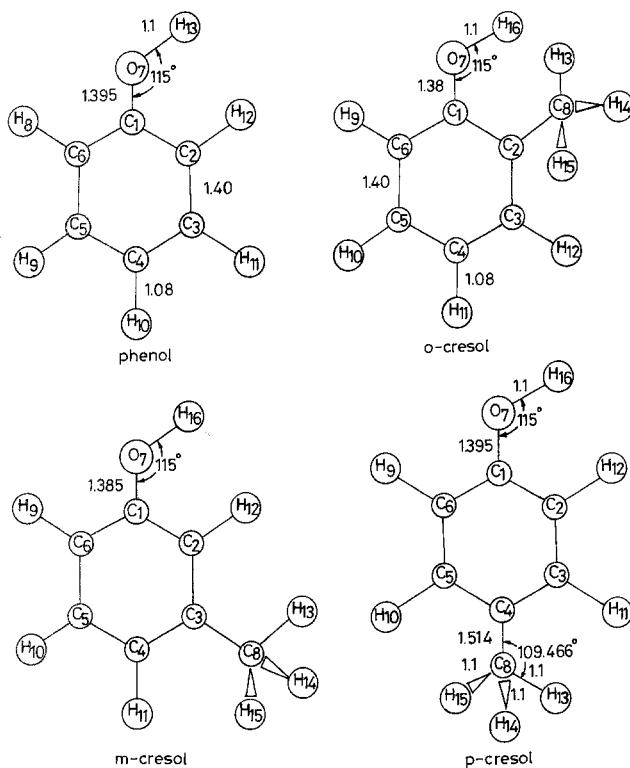


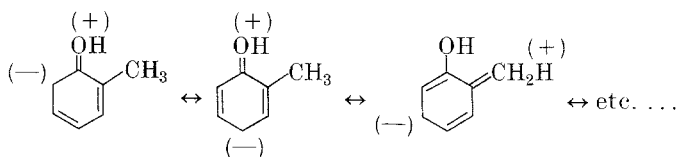
Fig. 2. Idealized geometry and numbering used for phenol and cresols calculations; modified data from Acta Cryst. **B 26**, 2086 (1970), *ibid.* **B 29**, 1011 (1973) and Z. Kristallogr. **119**, 273 (1963)

Before discussing the electronic structural aspects of cresols, it is worth comparing their electron density distribution along with their basic compounds—phenol and toluene. With phenol, the present CNDO/2 as well as the *ab initio* results<sup>32</sup> show that the hydroxyl group is a strong  $\Pi$ -donor to the benzene nucleus and this  $\Pi$ -donation is mainly from the p-type lone pair electrons of the oxygen atom.  $\sigma$ -electronwise the hydroxyl group is an acceptor from the phenyl ring (Table 2). The *ortho*-, *para*-directing influences of hydroxyl group is well brought out in our present results (Table 2). In toluene, the *ab initio* results of *Hehre* and co-workers<sup>32</sup> show the weak  $\Pi$ -donating nature of the methyl group and also its *ortho*-, *para*-directing tendency. These authors have emphasised the hyper-conjugative effect of the methyl group, involving the polarisation and transfer of  $\Pi$ -electrons. In the

present work the above concepts for phenol and toluene are extended to the cresols where both  $-\text{OH}$  and  $-\text{CH}_3$  groups are present simultaneously.

#### *ortho*-Cresol

In *ortho*-cresol the directing effects of hydroxyl and methyl groups oppose each other. That is, the available *ortho*- and *para*-positions of the methyl group are *meta*- to the hydroxyl group. Hence the excess electron density in these positions produced by the methyl group is likely to be annulled by the hydroxyl group. Table 2 clearly shows that the hydroxyl group dominates over the methyl group and that the positions  $\text{C}_3$  and  $\text{C}_5$  (*ortho*- and *para*- to the methyl group) are  $\Pi$ - and  $\sigma$ -electron deficient. The positions  $\text{C}_4$  and  $\text{C}_6$ , though *meta* to the methyl group, are still under the strong mesomeric influence of the hydroxyl group. These positions bear excess  $\Pi$ -electron but deficient  $\sigma$ -electron densities. The net  $\Pi$ -electron donation to the phenyl ring is considerable (0.070 esu) and is mainly due to the hydroxyl group. The results from the PPP-CI method also agree with the above facts (cf., Tables 3 and 4). It can be concluded that from reactivity point of view  $\text{C}_4$  and  $\text{C}_6$  are most favourable positions for electrophilic attack and  $\text{C}_3$  and  $\text{C}_5$  for nucleophilic attack. The above results support the following valence structures



contributing to the ground state of *ortho*-cresol.

#### *meta*-Cresol

In *meta*-cresol the directing effects of the methyl group and hydroxyl group reinforce and manifest at positions  $\text{C}_2$ ,  $\text{C}_4$  and  $\text{C}_6$ . All these positions bear excess  $\Pi$ -electron density and are deficient in  $\sigma$ -electron density. Our results show that in *meta*-cresol, the  $\sigma$ -donating capacity of the methyl group is overcompensated by the  $\sigma$ -withdrawing nature of the hydroxyl group. The total  $\Pi$ -electron accession to the phenyl ring is large (0.110 esu) and is higher than that of *ortho*-cresol. The position  $\text{C}_5$  is unique in that it is the only free *meta*-site to either groups. Naturally this position is  $\Pi$ -electron deficient and carries a net positive charge (Table 2). It is to be noted that our PPP-CI results also show the same trend in net charges and  $\Pi$ -bond orders (Tables 3 and 4).

Table 2. *Electron population and net charge data for phenol and cresols by CNDO/2 calculations*

Molecule	Electron density and net charge	Atoms*							
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	O <sub>7</sub>	C <sub>8</sub>
Phenol	π	0.951	1.060	0.975	1.037	0.976	1.057	1.942	
	σ	2.870	2.993	2.998	2.971	2.998	2.986	4.297	
	net	0.179	-0.053	0.026	-0.019	0.025	-0.043	-0.239	
Phenol		H <sub>8</sub>	H <sub>9</sub>	H <sub>10</sub>	H <sub>11</sub>	H <sub>12</sub>	H <sub>13</sub>		
	σ	0.990	1.003	1.004	1.005	0.995	0.878		
	net	0.009	-0.003	-0.004	-0.005	0.005	0.122		
o-Cresol		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	O <sub>7</sub>	C <sub>8</sub>
	π	0.969	1.034	0.999	1.028	0.989	1.051	1.938	0.974
	σ	2.865	2.981	2.992	2.988	2.994	2.990	4.303	3.035
net	0.166	-0.015	0.009	-0.016	0.017	-0.041	-0.241	-0.009	
o-Cresol		H <sub>9</sub>	H <sub>10</sub>	H <sub>11</sub>	H <sub>12</sub>	H <sub>13</sub>	H <sub>14</sub>	H <sub>15</sub>	H <sub>16</sub>
	σ	0.992	1.004	1.005	1.005	0.996	0.996	0.991	0.875
	net	0.008	-0.004	-0.005	-0.005	0.004	0.004	0.009	0.125



<i>m</i> -Cresol	Π	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	O <sub>7</sub>	C <sub>8</sub>
	σ	0.941	1.083	0.948	1.062	0.964	1.075	1.943	0.980
	net	2.876	2.979	2.990	2.974	3.005	2.987	4.298	3.040
		0.183	-0.062	0.062	-0.036	0.031	-0.062	-0.241	-0.020
		H <sub>9</sub>	H <sub>10</sub>	H <sub>11</sub>	H <sub>12</sub>	H <sub>13</sub>	H <sub>14</sub>	H <sub>15</sub>	H <sub>16</sub>
	σ	0.996	1.006	1.005	0.992	0.999	0.990	0.990	0.879
	net	0.004	-0.006	-0.005	0.008	0.001	0.010	0.010	0.121
<i>p</i> -Cresol	Π	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	O <sub>7</sub>	C <sub>8</sub>
	σ	0.965	1.048	0.999	1.007	1.009	1.046	1.944	0.976
	net	2.865	2.999	2.992	2.973	2.984	2.993	4.297	3.037
		0.170	-0.048	0.009	0.019	0.008	-0.038	-0.240	-0.013
		H <sub>9</sub>	H <sub>10</sub>	H <sub>11</sub>	H <sub>12</sub>	H <sub>13</sub>	H <sub>14</sub>	H <sub>15</sub>	H <sub>16</sub>
	σ	0.991	1.003	1.005	0.996	0.995	0.995	1.003	0.880
	net	0.009	-0.003	-0.005	0.004	0.005	0.005	-0.003	0.120

\* The numbering of atoms is given in Fig. 2.

Table 3. *Net charges in cresols derived from the PPP method*

Atoms	<i>ortho</i>	<i>meta</i>	<i>para</i>
C <sub>1</sub>	0.154	0.153	0.162
C <sub>2</sub>	0.015	-0.06	-0.060
C <sub>3</sub>	0.0042	0.027	-0.002
C <sub>4</sub>	-0.0273	-0.047	-0.031
C <sub>5</sub>	0.0028	0.003	0.01
C <sub>6</sub>	-0.0346	-0.068	-0.0548
O <sub>7</sub>	-0.189	-0.146	-0.147
C <sub>8</sub>	-0.178	-0.186	-0.185

Table 4. *Calculated  $\Pi$ -bond orders in cresols by CNDO/2\**

Bond	Cresol		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
C <sub>1</sub> —C <sub>2</sub>	0.6290 (0.6236)	0.6511 (0.6426)	0.6435 (0.6458)
C <sub>2</sub> —C <sub>3</sub>	0.6559 (0.6690)	0.6516 (0.6724)	0.6745 (0.6575)
C <sub>3</sub> —C <sub>4</sub>	0.6662 (0.6624)	0.6486 (0.6518)	0.6481 (0.6512)
C <sub>4</sub> —C <sub>5</sub>	0.6639 (0.6624)	0.6664 (0.6518)	0.6506 (0.6620)
C <sub>5</sub> —C <sub>6</sub>	0.6663 (0.6723)	0.6688 (0.6724)	0.6712 (0.6689)
C <sub>6</sub> —C <sub>1</sub>	0.6505 (0.6301)	0.6417 (0.6426)	0.6464 (0.6422)
C <sub>1</sub> —O <sub>7</sub>	0.2504 (0.2604)	0.2446 (0.2589)	0.2398 (0.2610)
C <sub>2</sub> —C <sub>8</sub> } C <sub>3</sub> —C <sub>8</sub> } C <sub>4</sub> —C <sub>8</sub> }	0.2122 (0.1944)	0.2134 (0.1941)	0.2108 (0.1950)

\* The values in parantheses refer to bond-orders calculated from the PPP-CI method.

Regarding reactivity, the positions C<sub>2</sub>, C<sub>4</sub> and C<sub>6</sub> are facile to electrophilic attack and C<sub>5</sub> to nucleophilic attack. In the light of the above results the contributing valence structures of the ground-state of *meta*-cresol can be formulated analogeous to the structures depicted for the *ortho*-isomer.

#### *para*-Cresol

In *para*-cresol, as in the case of the *ortho*-isomer, the directing effects of methyl and hydroxyl groups are in opposition to each other. Here also the hydroxyl group dominates over the methyl group. The

positions C<sub>2</sub> and C<sub>6</sub>, *ortho*- to hydroxyl group, are excess in  $\Pi$ -electron density and bear less  $\sigma$ -electron density; with net negative charges (Tables 2 and 3). The positions C<sub>3</sub> and C<sub>5</sub> (both *ortho* to the methyl group) though deficient in  $\Pi$ -electrons, show a net negative charge. The overall  $\Pi$ -donation to the phenyl ring is 0.068 esu and is almost the same as in *ortho*-cresol. Here again the CNDO/2 and PPP-CI results are in good agreement (Tables 3 and 4). As in the case of other isomers the reactivity of the positions C<sub>2</sub>, C<sub>6</sub>, C<sub>3</sub> and C<sub>5</sub> can be predicted. The valence structures are in analogy to the *ortho*-isomer.

Thus the CDNO/2 study quantitatively establishes the *ortho*-, *para*-directing characteristics of the hydroxyl and methyl groups when they are present simultaneously in a phenyl ring, with the —OH group as the more powerful  $\Pi$ -electron donor.

### Electronic Spectral Analysis

The computed values of electronic transitions along with their intensities ( $\log \epsilon$ ), both from conventional PPP and modified PPP-CI methods, and the experimentally observed spectra of all the three isomeric cresols are presented in Table 5. A reasonable assignment of

Table 5. *Electronic spectral data (theoretical and experimental) for cresols*

Molecule	Calculated values		Experimental values $\lambda_{\max}$ nm ( $\log \epsilon$ )
	PPP (conventional) $\lambda_{\max}$ nm ( $\log \epsilon$ )	PPP-CI (modified) $\lambda_{\max}$ nm ( $\log \epsilon$ )	
<i>o</i> -Cresol	267 (2.8)	275 (3.10)	279 (3.20)
			273 (3.30)
	223 (3.68)	233 (3.73)	215 (4.00)
	200 (4.46)	208 (4.43)	205 (3.80)
	189 (4.44)	195 (4.22)	
<i>m</i> -Cresol	266 (2.5)	273 (2.9)	279 (3.30)
			275 (3.30)
	219 (3.58)	227 (3.10)	219 (3.90)
	203 (4.45)	210 (4.42)	202.5 (4.00)
	189 (4.42)	197 (4.14)	
<i>p</i> -Cresol	267 (2.9)	274 (2.98)	285 (2.99)
			278 (3.10)
	225 (4.13)	234 (4.18)	225.5 (3.6)
	192 (4.13)	195 (4.20)	202 (3.5)
	187 (4.45)	194 (3.76)	

the observed electronic spectral bands for the three isomers based on our *PPP*-CI study will be attempted in this section.

The experimental absorption spectrum of *ortho*-cresol in methanol shows bands centered at 279, 273, 215 and 205 nm. The band at 273 nm is attributed to a transition involving a bonding orbital mainly contributed by the phenolic part of the molecule ( ${}_2\Pi$ ) and an antibonding orbital comprising solely of the phenyl part ( ${}_1\Pi^*$ ),  ${}_1\Pi^* \leftarrow {}_2\Pi$ . The band at 279 nm is a shoulder and is an asymmetric component of the 273 band and occurs due to a similar transition. In the case of phenol also a bunch of bands around 270 nm (namely 276, 271 and 266) are observed<sup>14</sup> and are explained to arise due to similar reasons. The present assignment of the 279 nm band in *ortho*-cresol is thus justified. The band at 215 nm is due to a transition involving  ${}_1\Pi$  and the antibonding  ${}_2\Pi^*$  orbitals of the phenolic part of the molecule ( ${}_2\Pi^* \leftarrow {}_1\Pi$ ). The highest energy band at 205 nm is due to the following two types of transitions:

- (i) from the bonding orbital  ${}_2\Pi$  to the antibonding orbital  ${}_2\Pi^*$  ( ${}_2\Pi^* \leftarrow {}_2\Pi$ ) and
- (ii) a transition comprising  ${}_1\Pi$  and  ${}_2\Pi^*$  ( ${}_2\Pi^* \leftarrow {}_1\Pi$ ).

*meta*-cresol in methanol gives four bands at 279, 275, 219 and 202.5 nm. The *PPP*-CI study reveals that the bands at 279 and 275 nm are identical to the corresponding bands in the *ortho*-isomer and hence similar transitions could be assigned. Likewise, the 219 and 202.5 nm bands correspond respectively to the 215 and 205 nm bands of the *ortho*-isomer and hence identical transitions are to be assigned. Except the highest energy band all the other bands in *meta*-cresol have suffered a red-shift from those of the *ortho*-cresol and phenol.

The *para*-isomer also gives four bands at 285, 278, 225.5 and 202 nm in methanol. Here also we observe enhanced red-shift compared to the other isomers and phenol. The assignment of these bands follows a similar pattern as in the case of other two isomers.

The present study confirms the findings of earlier workers<sup>22, 32</sup>, that the methyl group is a weak  $\Pi$ -donating moiety and that its presence in the phenyl ring of the cresols does not alter much the electronic spectra of the basic compound phenol. Unlike in nitrophenols<sup>21</sup> and hydroxy benzoic acids<sup>33</sup>, the spectral pattern of phenol changes only slightly in the cresols.

#### *Conformation and Dipole Moment*

In *ortho*- and *meta*-cresols, the *cis*- and *trans*-conformations of the hydroxyl hydrogen with respect to the methyl group have been considered for the CNDO/2 calculations. For *ortho*-cresol, the *cis*- and

Table 6. Dipole moment data for cresols

Cresol	<i>ortho (cis-)</i>			<i>meta (trans-)</i>			<i>para</i>			
	X	Y	Z	X	Y	Z	X	Y	Z	
Densities										
S, P	-0.503	0.393	-0.0	-0.016	0.469	0.0	-0.251	0.633	-0.0	
P, D	-0.754	0.808	-0.0	-0.843	0.823	-0.0	-0.823	0.821	-0.0	
Total	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Dipole moment	1.257	1.201	-0.0	-0.859	1.292	-0.0	-1.074	1.454	-0.0	
Experimental	1.738 D			1.552 D			1.808 D			
	1.25 to 1.60 D			1.30 to 1.60 D			1.50 to 1.70 D			

*trans*-conformations have total ground state energies  $-74.2536$  and  $-74.2517$  au, respectively. This shows that the *cis*-conformation is more stable than the *trans*- by an amount of  $0.0019$  au. This finding is in accordance with results published recently<sup>10</sup>. For the *meta*-isomer the ground state energies for *cis*- and *trans*-conformations are  $-74.2489$  and  $-74.2490$  au, respectively. Between the two geometrical isomers the difference in the values is too small to suggest any preference of one over the other. Hence we conclude that both *cis*- and *trans*-conformers are equally probable in the case of *meta*-cresol. The dipole moment of each isomer is calculated by the CNDO/2 method and is presented in Table 6 along with their experimentally available values<sup>34</sup>. A fair agreement between theory and experiment is seen justifying the use of CNDO/2 calculations for electronic structural studies in this type of compounds.

### Acknowledgements

One of the authors (*K. P. K. N.*) thanks the CSIR, New Delhi, for the award of a research fellowship and is indebted to the Inorganic and Physical Chemistry Department, Indian Institute of Science, Bangalore for permission to work as a short-term student, during which a part of this work was carried out.

### References

- <sup>1</sup> *Topsom R. D.*, Prog. Phys. Org. Chem. **12**, 1 (1976).
- <sup>2</sup> *Ehrensom S.*, *Brownlee R. T. C.*, *Taft R. W.*, Prog. Phys. Org. Chem. **10**, 1 (1973).
- <sup>3</sup> *Nishimoto K.*, *Forster L. S.*, Theoret. Chim. Acta **4**, 155 (1966).
- <sup>4</sup> *Bailey M. L.*, Theoret. Chim. Acta **13**, 56 (1969).
- <sup>5</sup> *Danihel I.*, *Kuthan J.*, Coll. Czech. Chem. Comm. **44**, 873 (1979).
- <sup>6</sup> *Gordon M. D.*, *Neumer J. F.*, J. Phys. Chem. **78**, 1868 (1974).
- <sup>7</sup> *Pople J. A.*, Proc. Phys. Soc. Ser. A **1955**, 69, 81.
- <sup>8</sup> *Dietrich S. W.*, *Jorgensen E. C.*, *Kollmann P. A.*, *Rothenberg R.*, J. Amer. Chem. Soc. **98**, 8310 (1976).
- <sup>9</sup> *Allinger N. L.*, *Maul J. J.*, *Hickey M. J.*, J. Org. Chem. **36**, 2747 (1971).
- <sup>10</sup> *Kudchadker S. A.*, *Wilholt R. C.*, *Zwolinski B. J.*, J. Phys. Chem. **82**, 245 (1978).
- <sup>11</sup> *Pullmann B.*, Quantum Mechanics of Molecular Conformations. London: J. Wiley. 1976.
- <sup>12</sup> *Brownlee R. T. C.*, *Taft R. W.*, J. Amer. Chem. Soc. **92**, 7007 (1970).
- <sup>13</sup> *Dobas I.*, *Eichler J.*, Coll. Czech. Chem. Comm. **38**, 2602 (1973).
- <sup>14</sup> *Campbell A. N.*, *Friesen R. J.*, Canad. J. Chem. **37**, 1296 (1959).
- <sup>15</sup> *Dearden J. C.*, *Forbes W. F.*, *ibid.* **38**, 897 (1960).
- <sup>16</sup> *Kammerer H.*, *Lewenz W.*, Spectrochim. Acta **24A**, 2059 (1968).
- <sup>17</sup> *Ito M.*, J. Mole. Spectroscopy **4**, 134 (1960).
- <sup>18</sup> *Pople J. A.*, Trans. Faraday Soc. **49**, 1375 (1953).

- 19 *Pariser R., Parr R. G.*, J. Chem. Phys. **21**, 466, 767 (1953).
- 20 *Namboodiri K. P. K., Viswanathan S., Ganesan R., Bhasu V. C. J.*, J. Comp. Chem., in press.
- 21 *Bhasu V. C. J., Sathyanarayana D. N.*, Phosphorus and Sulfur **8**, 171 (1980).
- 22 *Bhasu V. C. J.*, Ph. D. Thesis, Indian Institute of Science, Bangalore, India, 1977.
- 23 *Brownlee R. T. C., Taft R. W.*, J. Amer. Chem. Soc. **90**, 6537 (1968).
- 24 *Platt J. R.*, Systematics of the Electronic Spectra of Conjugated Molecules, Paper No. 32. New York: Wiley. 1964.
- 25 *Pople J. A., Beveridge D. L.*, Approximate Molecular Orbital Theory, appendix-program. New York: McGraw-Hill. 1970.
- 26 *Nishimoto K., Forster L. S.*, Theor. Chim. Acta **3**, 407 (1965).
- 27 *Nishimoto K., Mataga N.*, Z. Physik. Chem. (Frankfurt am Main) **12**, 335 (1957).
- 28 *Fabian J.*, Tetrahedron **29**, 2449 (1973).
- 29 *Dewar M. J. S., Morita T.*, J. Amer. Chem. Soc. **91**, 796 (1969).
- 30 *Zahradnik R., Tesarova I., Pancir J.*, Coll. Czech. Chem. Comm. **36**, 2867 (1971).
- 31 *Vogel A. I.*, A Text Book of Practical Organic Chemistry, pp. 169, 614, 677. London: E. L. B. S. 1968.
- 32 *Hekre W. J., Radom L., Pople J. A.*, J. Amer. Chem. Soc. **94**, 1496 (1972).
- 33 *Namboodiri K. P. K., Viswanathan S., Ganesan R., Bhasu V. C. J.*, in preparation.
- 34 *McClellan A. L.*, Tables of Experimental Dipole Moment, Vol. I. San Francisco: Freeman. 1963; Vol. II. California: Arhara Enterprises. 1974.