

# Competition between electron-donor and electron-acceptor substituents in nitrotoluene isomers: a photoelectron spectroscopy and *ab initio* investigation

† **Electronic Supplementary Information**

Flaminia Rondino,<sup>†</sup> Daniele Catone,<sup>‡</sup> Giuseppe Mattioli,<sup>\*,¶</sup> Aldo Amore  
Bonapasta,<sup>¶</sup> Paola Bolognesi,<sup>§</sup> Anna Rita Casavola,<sup>§</sup> Marcello Coreno,<sup>§</sup> Patrick  
O'Keeffe,<sup>§</sup> and Lorenzo Avaldi<sup>§</sup>

*ENEA Centro Ricerche di Frascati, Unità Tecnica Sviluppo di Applicazioni delle Radiazioni, Via  
E. Fermi 45, I-00044 Frascati (RM), Italy, Istituto di Struttura della Materia del CNR, Via del  
Fosso del Cavaliere 100, I-00133 Roma, Italy, Istituto di Struttura della Materia del CNR, Via  
Salaria Km 29.300, I-00015 Monterotondo Stazione (RM), Italy, and Istituto di Metodologie  
Inorganiche e dei Plasmi del CNR, Via Salaria Km 29.300, I-00015 Monterotondo Stazione (RM),  
Italy*

E-mail: giuseppe.mattioli@ism.cnr.it

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\*To whom correspondence should be addressed

<sup>†</sup>ENEA

<sup>‡</sup>CNR-ISM1

<sup>¶</sup>CNR-ISM2

<sup>§</sup>CNR-IMIP

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## **1 Valence Spectra and Molecular Orbitals of the Nitrotoluene Isomers**

The valence spectra of the three nitrotoluene isomers have been taken by using the same experimental setup described in the main text. The spectra have been measured at 50 eV photon energy with an overall resolution of 120 meV. Energy calibration and resolution of the spectra was achieved by adding a small amount of He. The spectra are displayed in Figure S1 together with the calculated ionisation energies (IEs) marked with bars. All the spectra show two sharp and well resolved peaks at lower IE, the former assigned to the HOMO (highest occupied molecular orbital) and HOMO-1 contributions, the latter to the HOMO-2, HOMO-3 and HOMO-4 contributions, respectively, followed by an extended region of overlapped photoelectron bands up to about 20 eV. The following discussion is focused on the properties of the above low energy peaks and of the related molecular orbitals.

The measured IE values have been determined by using Gaussian functions to fit the spectra. The corresponding results are reported in Table SI, together with the corresponding calculated values, estimated by means of the outer valence Green's function (OVGF) method and a 6-311G\*\* basis set. This theoretical approach includes a treatment of electron correlation in the framework of a one-particle hole model for the ionisation. All the calculated pole strengths in the OVGF calculation are greater than 0.8, as shown in Table SI, that is, within the limits of the OVGF

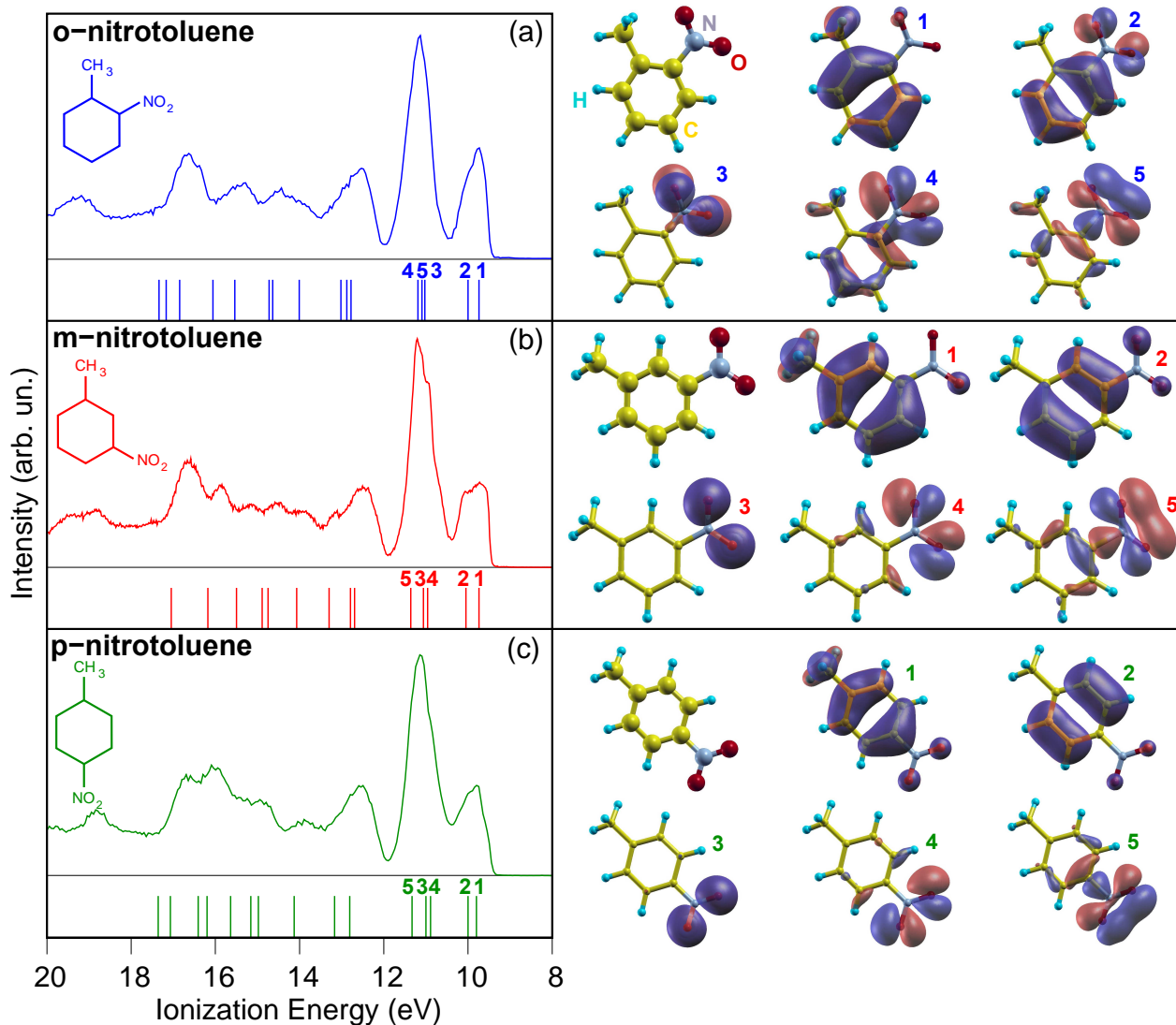


Figure S1: Valence photoemission spectra of *o*-nitrotoluene (A), *m*-nitrotoluene (B), and *p*-nitrotoluene (C). The spectra have been taken at 50 eV photon energy with an overall resolution of 120 meV. The bars below the spectra correspond to theoretical estimates of ionisation peaks calculated by using the OVFG method and a 6-311g(d,p) basis set. low energy (1-5) peaks can be directly assigned to the molecular orbitals shown in the right panels of the figure. The corresponding ionisation energy values are also reported in Table S1.

**Table SI: Measured and Calculated Ionisation Energy Values of Nitrotoluene Isomers.** Measured ionisation energy values, determined by using Gaussian functions to fit the spectra, are reported in the “Exp.” columns; the corresponding calculated values, obtained by using the OVGF method and a 6-311g(d,p) basis set, are reported in the “OVGF” columns. All the ionisation energy values are in eV, in agreement with data shown in Figure S1. The pole strength of theoretical excitations (see the text for details) are also reported in the “PS” columns. The bracketed values in column “MO” correspond to the molecular orbitals shown in Figure S1.

MO	<i>o</i> -nitrotoluene			<i>m</i> -nitrotoluene			<i>p</i> -nitrotoluene		
	OVGF	PS	Exp.	OVGF	PS	Exp.	OVGF	PS	Exp.
(1) HOMO	9.74	0.88	9.74	9.74	0.89	9.66	9.80	0.88	9.72
(2) HOMO-1	10.00	0.88	10.01	10.05	0.88	10.10	10.00	0.89	10.01
(3) HOMO-2	11.03	0.85	10.98	11.06	0.85	10.91	11.00	0.84	10.92
(4) HOMO-3	11.19	0.88	11.16	10.96	0.88	11.20	10.89	0.88	11.11
(5) HOMO-4	11.09	0.87	11.38	11.36	0.88	11.28	11.33	0.88	11.21

approximation.<sup>1</sup> The line-up of molecular orbitals is also in agreement with the results of previous calculation performed at a 6-31G\* level of the theory.<sup>2</sup>

**Table SII: Total Energies of Nitrotoluene Isomers.** The total energies and relative stabilities of the nitrotoluene isomers are reported. B3LYP (OVGF) calculations have been performed by using a 6-311++g(d,p) (6-311g(d,p)) basis set.

Species	E(B3LYP) (eV)	$\Delta E$ (eV)	E(OVGF) (eV)	$\Delta E$ (eV)
<i>o</i> -nitrotoluene	-12958.321	+0.132	-12922.153	+0.074
<i>m</i> -nitrotoluene	-12958.438	+0.015	-12922.227	0
<i>p</i> -nitrotoluene	-12958.453	0	-12922.212	+0.015

The molecular structures of the three nitrotoluene isomers are shown in the right panels of Figure S1. As discussed in the main text, the NO<sub>2</sub> group is coplanar with the benzene ring in the cases of the *m*- and *p*-nitrotoluene, while the proximity of the CH<sub>3</sub> group induces its twisting in the case of *o*-nitrotoluene. Such a twisting is responsible for the lower stability of the *o*- molecule with respect to the *m*- and *p*- ones, which has been found in the cases of both B3LYP and OVGF calculations, as reported in Table SII. Slight changes of the energy ordering of *m*- and *p*-nitrotoluene have been found when comparing the B3LYP calculations with the more accurate OVGF ones. Besides the inhibition of the  $\pi$ -conjugation of the NO<sub>2</sub> group in the case of *o*-nitrotoluene, discussed in the main text, the structural differences between isomers lead to modifications of the outer molecular orbitals. We have found that the *p*-nitrotoluene HOMO is the most stable frontier

orbital, at variance with previous findings by Kobayashi et al.,<sup>3</sup> while the *o*- and *m*-nitrotoluene HOMOs are characterised by almost identical values. In general, the spatial localisation of frontier orbitals reflects the molecular symmetry, still appreciable in the case of *p*-nitrotoluene, very low (if the position of the three H atoms belonging to the methyl group is neglected) in the case of *m*-nitrotoluene, completely disrupted by NO<sub>2</sub> twisting in the case of *o*-nitrotoluene. If we focus on the HOMOs, labelled 1 in Figure S1, we can observe a different distribution of charge density, almost fully localised on the CH<sub>3</sub> group and on the benzene ring in the case of the *o*-nitrotoluene, more involving the NO<sub>2</sub> group in the case of the *m*- and *p*- isomers. An opposite tendency characterises the HOMO-1 orbitals instead, labelled 2 in Figure S1, with the NO<sub>2</sub> moiety appreciably contributing to the HOMO-1 in the case of the *o*- isomer. Moreover, changes in the ordering of HOMO-2, HOMO-3 and HOMO-4 orbitals of the *o*- isomer with respect to the *m*- and *p*- ones are found, with the orbital labelled 4 in Figure S1 and Table SI, mainly centered on the NO<sub>2</sub> group, which is stabilised by a wider delocalisation on the benzene ring and on the neighbouring CH<sub>3</sub> group in the case of *o*-nitrotoluene.

## 2 N(1s) and O(1s) XPS

The N(1s) and O(1s) core photoemission spectra of nitrotoluenes have been measured using incident photon beams of 495 eV and 628 eV, with an overall resolution of 0.46 eV and 0.53 eV, respectively. The kinetic energy of about 100 eV above the ionisation threshold in the photoelectron spectra guarantees that final state effects, e. g., the post collisional effects (PCI)<sup>4</sup> that shift and modify the shape of the peaks, can be neglected in the data analysis. The XPS spectra were calibrated using a mixture of the molecule under investigation and of a calibration gas with well-known XPS lines in the same ionisation energy (IE) range, that is, CO<sub>2</sub> (O(1s) at 541.3 eV)<sup>5</sup> and N<sub>2</sub> (N(1s) at 409.9 eV).<sup>6,7</sup>

The analysis of N(1s) and O(1s) IE values, albeit less interesting than C(1s) one, provides similar insight into the properties of the three nitrotoluene isomers. First of all, if we compare all

Table SIII: N(1s) and O(1s) XPS ionisation energies (IEs) of *o*-nitrotoluene (A), *m*-nitrotoluene (B), and *p*-nitrotoluene (C). The N(1s) and O(1s) IE values are calculated by Gaussian fitting the corresponding spectra, acquired at 495 eV and 628 eV, respectively. NO<sub>2</sub> and nitrobenzene values are taken from Jolly et al.<sup>8</sup>

Species	N(1s) IE (eV)	O(1s) IE (eV)
NO <sub>2</sub>	541.3	412.9
nitrobenzene	538.63	411.73
<i>o</i> -nitrotoluene	538.70±0.01	411.64±0.004
<i>m</i> -nitrotoluene	538.64±0.01	411.56±0.004
<i>p</i> -nitrotoluene	538.45±0.01	411.54±0.004

the nitrotoluene values with the corresponding values measured in the case of a free NO<sub>2</sub> molecule, we notice the strong electron donor behaviour of the aryl groups, acting as “substituents” of NO<sub>2</sub>. Both the N(1s) and O(1s) core holes are more efficiently screened with the contribution of the aryl groups (benzyl and tolyl in the cases of nitrobenzene and nitrotoluenes, respectively). A finer comparison of nitrobenzene and nitrotoluenes results provide further proofs of the I+/R- effect of the CH<sub>3</sub> group, extended to the screening of core holes induced in the NO<sub>2</sub> substituent. The R- effect is indeed clearly appreciable in the case of *p*-nitrotoluene, showing the lowest N(1s) and O(1s) IE values. The *m*- isomer is characterised by IE values quite similar to the nitrobenzene ones, due to the fact that the methyl group holds the non-resonant *meta* position. The *o*-nitrotoluene molecule, finally, is characterised by an attenuated R- contribution of the whole aryl system to the screening of the N(1s) and O(1s) core holes, due to the twisting of the nitro group, and show therefore IE values higher than the nitrobenzene ones.

### 3 Comparison of Theoretical IE Values in the Case of Toluene

Calculated C(1s) IE values in the case of toluene are reported in Table SIV. Present results, obtained in the plane-wave/pseudopotential approach (PW column in Table SIV) discussed in detail in the main text, are compared to previous results obtained by using a different localized basis set/all electron approach (GTO column in Table SIV).<sup>9</sup> Such *ab initio* results have been also compared to further results obtained by fitting the XPS spectra with theoretically calculated lineshapes

(FIT column in Table SIV).<sup>9</sup> The very good agreement between GTO and FIT results is obtained after allowing for the correction of a large systematic error.

Table SIV: **Toluene C(1s) IE values.** C(1s) IE values calculated for all the inequivalent positions of toluene using the present plane-wave based approach (PW column), as opposite to previous results obtained by using localized basis sets (GTO column).<sup>9</sup> Previous results obtained by fitting the XPS spectrum (FIT column)<sup>9</sup> are also shown for comparison.

Atom	PW IE value (eV)	GTO IE value (eV)	FIT IE value (eV)
C0 (CH <sub>3</sub> )	290.88	290.69	290.70
C1	290.53	290.43	290.41
C2,6	290.23	290.09	290.11
C3,5	290.34	290.21	290.25
C4	290.25	290.11	290.18

## 4 Atom Coordinates and Total Energies of Nitrotoluene Isomers

The optimized geometries of the three nitrotoluene isomers are provided in the following in order to ensure the full reproducibility of the achieved results. The corresponding Total Energy values are also displayed in Table SII. The calculations have been performed by using the Gaussian 03 package,<sup>10</sup> as detailed in the main text.

### *o*-nitrotoluene

Energy= -476.198794178 (Hartree a.u.)

Final structure in terms of initial Z-matrix:

C

C,1,B1

C,2,B2,1,A1

C,3,B3,2,A2,1,D1,0

C,4,B4,3,A3,2,D2,0

C,1,B5,2,A4,3,D3,0

H,3,B6,2,A5,1,D4,0

H,4,B7,3,A6,2,D5,0

H,5,B8,4,A7,3,D6,0

H,6,B9,1,A8,2,D7,0

C,1,B10,6,A9,5,D8,0

H,11,B11,1,A10,6,D9,0

H,11,B12,1,A11,6,D10,0

H,11,B13,1,A12,6,D11,0

N,2,B14,1,A13,6,D12,0

O,15,B15,2,A14,1,D13,0

O,15,B16,2,A15,1,D14,0

Variables:

B1=1.4054473

B2=1.39447293

B3=1.3873102

B4=1.39370772

B5=1.40155785

B6=1.08134353

B7=1.08315425

B8=1.08406266

B9=1.08429816

B10=1.50804195

B11=1.09126267

B12=1.09166413



B13=1.09128251

B14=1.47923142

B15=1.22544007

B16=1.22565831

A1=122.79029551

A2=119.65892644

A3=119.23095092

A4=115.75118034

A5=118.8357912

A6=120.01591053

A7=120.16301894

A8=118.25815046

A9=119.05140644

A10=112.12290572

A11=111.16719062

A12=109.55108172

A13=121.22661394

A14=117.57974211

A15=118.08009912

D1=1.25291264

D2=-1.23220962

D3=-0.17153643

D4=-178.9307774

D5=179.06572804

D6=-179.48719681

D7=178.95330277

D8=-179.80037617

D9=132.08444615

D10=-108.88753623

D11=11.36207288

D12=-179.95200079

D13=154.10185436

D14=-26.63863928

***m*-nitrotoluene**

Energy= -476.203058496 (Hartree a.u.)

Final structure in terms of initial Z-matrix:

C

C,1,B1

C,2,B2,1,A1

C,3,B3,2,A2,1,D1,0

C,4,B4,3,A3,2,D2,0

C,1,B5,2,A4,3,D3,0

H,1,B6,6,A5,5,D4,0

H,2,B7,1,A6,6,D5,0

H,3,B8,2,A7,1,D6,0

C,6,B9,1,A8,2,D7,0

H,10,B10,6,A9,1,D8,0

H,10,B11,6,A10,1,D9,0

H,10,B12,6,A11,1,D10,0

N,4,B13,3,A12,2,D11,0

O,14,B14,4,A13,3,D12,0

O,14,B15,4,A14,3,D13,0

H,5,B16,4,A15,3,D14,0

Variables:

B1=1.3930902

B2=1.39164803

B3=1.38957401

B4=1.39171191

B5=1.40164561

B6=1.08521115

B7=1.08359973

B8=1.080845

B9=1.50917754

B10=1.09122978

B11=1.09492345

B12=1.09283621

B13=1.4809015

B14=1.22497317

B15=1.22471924

B16=1.08187167

A1=120.39072668

A2=117.89086555

A3=122.46181436

A4=121.39227902

A5=119.23529012

A6=119.97151008

A7=122.12189908

A8=120.81484697

A9=111.39765841

A10=110.83877617

A11=111.23994007

A12=118.86665786

A13=117.7564049

A14=117.68045112

A15=119.12930386

D1=0.03433334

D2=-0.01158116

D3=0.08032379

D4=179.67179946

D5=179.9039074

D6=179.85472312

D7=178.98930621

D8=164.30197573

D9=-75.83554481

D10=43.54634883

D11=179.79361269

D12=-179.76675791

D13=0.26346554

D14=179.78625095

### ***p*-nitrotoluene**

Energy= -476.203632381 (Hartree a.u.)

Final structure in terms of initial Z-matrix:

C

C,1,B1

C,2,B2,1,A1

C, 3, B3, 2, A2, 1, D1, 0

C, 4, B4, 3, A3, 2, D2, 0

C, 1, B5, 2, A4, 3, D3, 0

H, 1, B6, 6, A5, 5, D4, 0

H, 4, B7, 3, A6, 2, D5, 0

H, 5, B8, 4, A7, 3, D6, 0

C, 3, B9, 2, A8, 1, D7, 0

H, 10, B10, 3, A9, 2, D8, 0

H, 10, B11, 3, A10, 2, D9, 0

H, 10, B12, 3, A11, 2, D10, 0

N, 6, B13, 1, A12, 2, D11, 0

O, 14, B14, 6, A13, 1, D12, 0

O, 14, B15, 6, A14, 1, D13, 0

H, 2, B16, 1, A15, 6, D14, 0

Variables:

B1=1.38806928

B2=1.40263713

B3=1.39966016

B4=1.39091082

B5=1.39249851

B6=1.08129252

B7=1.08430211

B8=1.08132224

B9=1.50748212

B10=1.09409119

B11=1.09415616

B12=1.09099806

B13=1.47599965

B14=1.22546745

B15=1.22555762

B16=1.08478109

A1=121.25412131

A2=118.41137137

A3=121.25958166

A4=118.70386822

A5=119.63130743

A6=119.54100476

A7=121.62453556

A8=120.44149654

A9=110.98162833

A10=110.96431523

A11=111.49992462

A12=119.15506473

A13=117.74301362

A14=117.72340512

A15=119.19332379

D1=0.00764854

D2=-0.00400123

D3=-0.0053875

D4=179.99285691

D5=179.98936872

D6=179.9966977

D7=-179.96988806

D8=-59.14554588  
D9=59.92282184  
D10=-179.62698813  
D11=-179.99642637  
D12=179.99123991  
D13=-0.00644988  
D14=179.99543725

Plane-wave/pseudopotential calculations have been performed by using the Quantum ESPRESSO suite,<sup>11</sup> as detailed in the main text. The norm-conserving C.blyp-mt.UPF, N.blyp-mt.UPF, O.blyp-mt.UPF, H.blyp-vbc.UPF pseudopotentials employed to carry out B3LYP ground state calculations are available for download in the Quantum ESPRESSO pseudopotential library. We note that plane-wave/pseudopotential energies cannot be compared with the above all-electron energies. The calculations yielded the following ground state properties:

### ***o*-nitrotoluene**

Final energy and structure in terms of Cartesian coordinates:

Final energy = -173.0461539399 (Rydberg a.u.)

Begin final coordinates

ATOMIC\_POSITIONS (angstrom)

C 5.562073288 6.009576524 5.433429719

C 6.151385864 4.750941932 5.426425480

C 5.358709400 3.621262580 5.430882399

C 3.978617550 3.762913313 5.432208589

C 3.408537605 5.024496135 5.425916493

C 4.173072955 6.191851811 5.429098843

H 2.335082849 5.119442061 5.414286367

H 3.344529897 2.891744379 5.431150449  
H 7.223585196 4.684455177 5.422479957  
H 5.812199406 2.644542989 5.428366161  
C 3.461448324 7.515334796 5.401003812  
H 3.574771689 8.045660602 6.341316171  
H 2.404670293 7.352682325 5.216418632  
H 3.854830897 8.171702613 4.632189724  
N 6.490769840 7.152161931 5.438254090  
O 6.060213104 8.257746608 5.774640548  
O 7.661726535 6.942004143 5.114946595  
End final coordinates

***m*-nitrotoluene**

Final energy and structure in terms of Cartesian coordinates:

Final energy = -173.0551314096 (Rydberg a.u.)

Begin final coordinates

ATOMIC\_POSITIONS (angstrom)

C 5.494447099 6.090106810 5.430191891  
C 6.118033528 4.853745792 5.433283746  
C 5.409477340 3.664966966 5.428926245  
C 4.026436742 3.735357605 5.430394354  
C 3.386177602 4.966629479 5.430254904  
C 4.106807775 6.160265080 5.424744356  
H 2.308041973 5.002161229 5.424918289  
H 3.445948274 2.828108251 5.423999637  
H 6.098158679 6.979910476 5.425958774  
H 5.933583690 2.727212509 5.422797393



```
C 3.406058038 7.491277637 5.421579797
H 3.181718318 7.821714624 6.434697975
H 2.466237181 7.436471218 4.880693908
H 4.020863616 8.255477110 4.956954000
N 7.590014406 4.807385884 5.434487777
O 8.200047352 5.877737515 5.436632008
O 8.132463961 3.701442301 5.434456144
End final coordinates
```

### ***p*-nitrotoluene**

Final energy and structure in terms of Cartesian coordinates:

Final energy = -173.0566893128 (Rydberg a.u.)

Begin final coordinates

ATOMIC\_POSITIONS (angstrom)

```
C 5.468272762 6.023377476 5.423963653
C 6.084984016 4.785124775 5.438690649
C 5.294931082 3.647851757 5.446501722
C 3.911554547 3.724962696 5.438824003
C 3.314704538 4.971837631 5.424269512
C 4.078229915 6.139145493 5.415508892
H 2.238422287 5.039666361 5.419792027
H 3.329954064 2.821417032 5.432983280
H 7.155574321 4.688938154 5.433089402
H 6.075938317 6.914076854 5.419591356
C 3.416867269 7.488175778 5.415462470
H 3.205945089 7.816705222 6.432786209
H 2.472528566 7.463209857 4.880630713
```

H 4.050430493 8.239222185 4.954944014  
N 5.934987843 2.326818936 5.448293684  
O 7.166509664 2.278755198 5.448868093  
O 5.204377051 1.333918190 5.446365180  
End final coordinates

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