



*Supplement of*

**Investigations into the gas-phase photolysis and OH radical kinetics of nitrocatechols: implications of intramolecular interactions on their atmospheric behaviour**

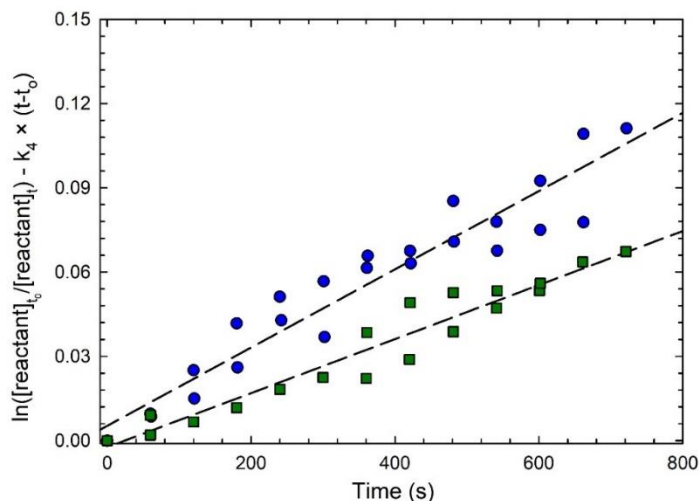
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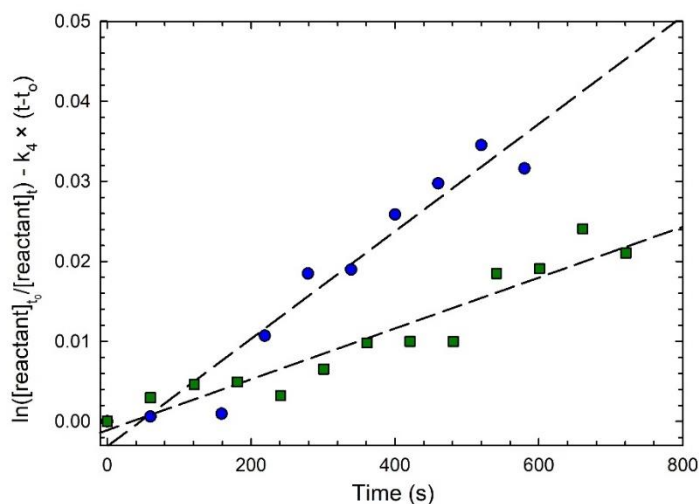
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The present supplementary material (SM) aims to provide assistance for the obtained results with additional information supporting the reliable conclusions of the research study. The SM provides graphical illustration, details related to recorded data and instrumentation.

**Figure S1** and **Figure S2** present the gas-phase photolysis plots for 3-nitrocatechol and 5-methyl-3-nitrocatechol at 365 nm, and gas-phase photolysis plots for 4-nitrocatechol and 4-methyl-5-nitrocatechol at 254 nm. The photolysis rate constants were corrected for the wall loss ( $k_4$ ), according to the reaction sequence presented in the manuscript.



**Figure S1:** Kinetic plots according to the photolysis of (●) 3NCAT and (■) 5M3NCAT at 365 nm corrected for the wall loss, with  $k_4 = (3.2 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$  (see details in the manuscript text).



**Figure S2:** Kinetic plots according to the photolysis at 254 nm of (●) 4NCAT and (■) 4M5NCAT corrected for the wall loss, with  $k_4 = (0.7 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$  (see details in the manuscript text).

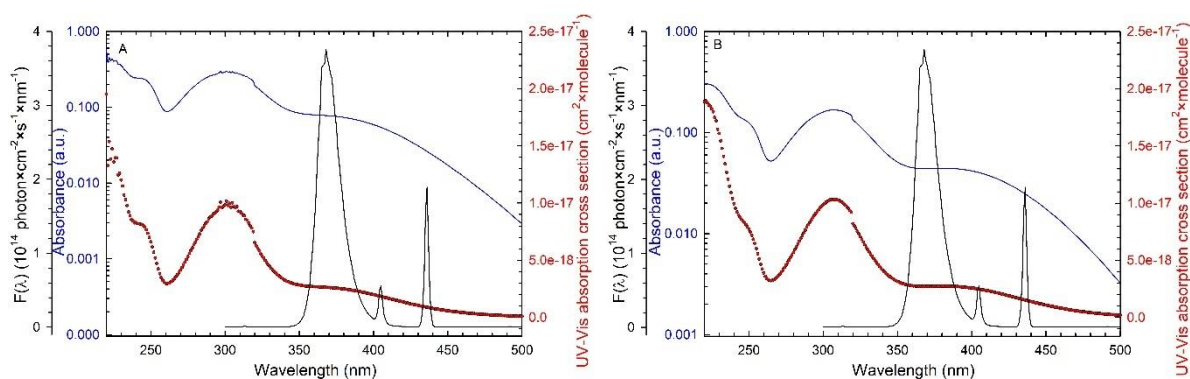
**Figure S3** illustrates the UV-Vis spectra for 3-nitrocatechol and 5-methyl-3-nitrocatechol and the calculated UV-Vis cross-sections. For comparison, the emission spectra of the used lamps emitting light in the range of 310 - 460 nm within maxima at 365 nm and recorded with an LI-COR spectroradiometer at a resolution of 1 nm inside the ESC-Q-UAIC chamber is given. The UV-Vis spectra for 3-nitrocatechol and 5-

methyl-3-nitrocatechol from Figure S3 A and S3 B shows two intense absorption bands ( $\lambda < 250$  and  $260 < \lambda < 350$ ) corresponding to a  $\pi\text{-}\pi^*$  transition and one absorption band with a smaller intensity placed from 350 to 450 nm corresponding to  $n\text{-}\pi^*$  transition in the 3-nitrocatechol molecule. **Table S1** shows the values for the absorption cross sections ( $\sigma$ ) calculated in the 350-400 nm range (similar with the band intensity range emitted by the 365 nm lamps in the ESC-Q-UAIC reactor).

UV-Vis spectra of 3-nitrocatechol and 5-methyl-3-nitrocatechol, recorded in aqueous solution for the 220 - 500 nm wavelength range, were registered using a SPECORD 210 Plus UV-Vis spectrophotometer from Analytic Jena. Stock solution of 0.950 mg/mL of 3NCAT and 0.568 mg/mL of 5M3NCAT were used to obtain solutions by dilution over a large concentration range from  $3.69 \times 10^{15}$  to  $2.95 \times 10^{17} \text{ cm}^{-3}$ . The solution with five different concentrations were used to evaluate the absorption cross-sections.

Assuming similar cross-sections in the gas-phase with those in the aqueous solution, for the 350-400 nm photolytic range, an average quantum yield can be estimated using **equation S<sub>eq 1</sub>** (Hofzumahaus et al., 1999). Using a boxcar integration method, the overall average quantum yields for this photolytic range ( $\Phi_{350-400}$ ) are:  $(7.707 \pm 0.737) \times 10^{-3}$  for 3NCAT and  $(4.858 \pm 0.464) \times 10^{-3}$  for 5M3NCAT. The overall errors include contributions from the solution preparation, UV-Vis spectra recording and the photolysis value. The quantum yields values from the present study should be considered with caution, due to the charge transfer band of nitroaromatics which is known to undergo a considerable redshift by the change from gas-phase to solution and in thin film, and due to use of water as a solvent which is expected to provide largest shifts (Bejan, 2006; Reichardt and Welton, 2010).

$$-\frac{d[A]}{dt} = [A] \times J = [A] \times \int_{\lambda} \phi(\lambda) \sigma(\lambda) F(\lambda) d\lambda \quad \text{S}_{\text{eq}1}$$



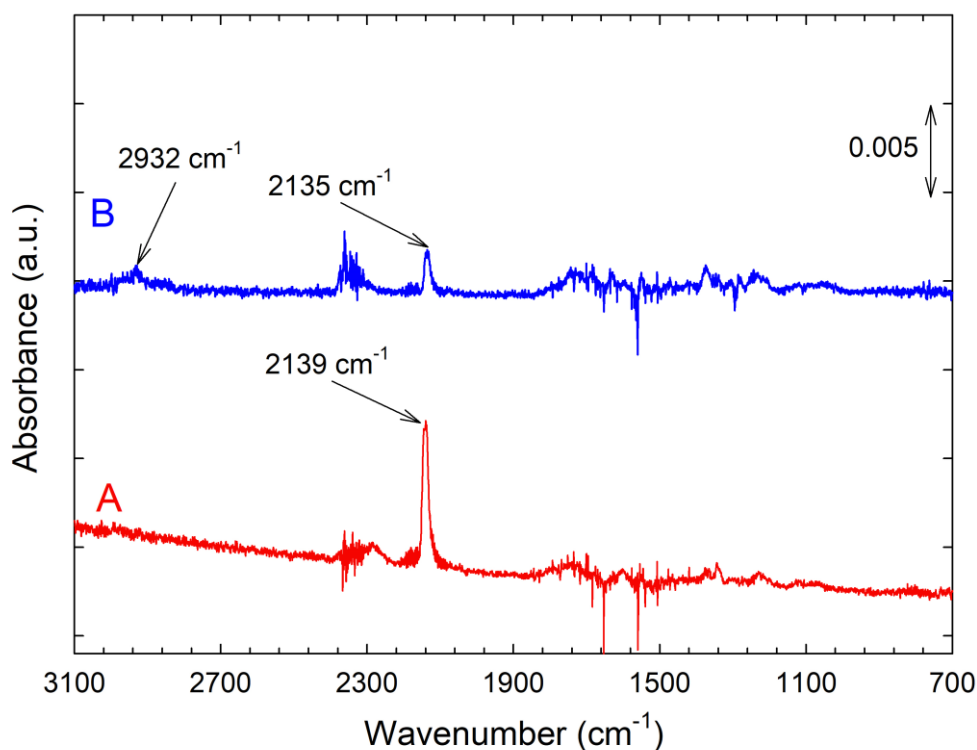
**Figure S3:** UV-Vis absorbance spectra of (A) 3NCAT and (B) 5M3NCAT in aqueous solution with the corresponding UV-Vis absorption cross sections (base 10) for 3NCAT and 5M3NCAT in the 220-500 nm range, along with the emission spectrum in the range of 300-500 nm of the Philips TL-DK 36W lamps.

**Table S1:** UV-Vis absorption cross section of 3NCAT and 5M3NCAT in aqueous solution in the 350-500 nm spectral range (base 10) and the mean irradiance values of the actinic lamps ( $2\pi$  sr acquisition mode) inside the ESC-Q-UAIC reactor.

$\lambda$ (nm)	$\sigma_{3NCAT} \times 10^{18}$ ( $\text{cm}^2 \times \text{molecule}^{-1}$ )	$\sigma_{5M3NCAT} \times 10^{18}$ ( $\text{cm}^2 \times \text{molecule}^{-1}$ )	$E \times 10^{-11}$ ( $\text{photon} \times \text{cm}^{-2} \times \text{nm}^{-1} \times \text{s}^{-1}$ )	$\lambda$ (nm)	$\sigma_{3NCAT} \times 10^{18}$ ( $\text{cm}^2 \times \text{molecule}^{-1}$ )	$\sigma_{5M3NCAT} \times 10^{18}$ ( $\text{cm}^2 \times \text{molecule}^{-1}$ )	$E \times 10^{-11}$ ( $\text{photon} \times \text{cm}^{-2} \times \text{nm}^{-1} \times \text{s}^{-1}$ )
350	2.82	3.16	1.30	426	1.16	1.87	3.19
351	2.80	3.10	0.82	427	1.13	1.83	3.43
352	2.78	3.04	1.22	428	1.10	1.80	3.26
353	2.76	3.00	1.01	429	1.08	1.77	3.25
354	2.74	2.95	1.58	430	1.05	1.73	3.35
355	2.73	2.91	0.73	431	1.02	1.70	7.84
356	2.72	2.88	0.88	432	0.99	1.67	38.13
357	2.71	2.85	0.49	433	0.97	1.63	122.32
358	2.70	2.82	0.78	434	0.94	1.60	327.30
359	2.69	2.80	0.27	435	0.91	1.56	773.47
360	2.68	2.78	0.72	436	0.89	1.53	946.83
361	2.67	2.77	1.51	437	0.86	1.49	564.43
362	2.67	2.75	4.57	438	0.83	1.46	209.74
363	2.66	2.74	8.52	439	0.81	1.42	71.36
364	2.66	2.73	6.50	440	0.79	1.39	14.72
365	2.65	2.73	2.49	441	0.76	1.36	3.00
366	2.64	2.73	1.22	442	0.74	1.33	2.34
367	2.63	2.72	0.57	443	0.72	1.30	2.13
368	2.63	2.72	0.87	444	0.70	1.27	2.30
369	2.62	2.72	0.77	445	0.68	1.24	2.16
370	2.61	2.72	0.54	446	0.66	1.21	2.22
371	2.60	2.73	0.37	447	0.64	1.18	1.98
372	2.59	2.73	0.51	448	0.62	1.15	1.99
373	2.58	2.73	0.85	449	0.60	1.11	1.97
374	2.57	2.73	0.82	450	0.58	1.08	1.96
375	2.56	2.74	0.48	451	0.56	1.05	2.01
376	2.54	2.74	0.75	452	0.54	1.03	1.96
377	2.53	2.74	0.87	453	0.53	1.00	1.79
378	2.51	2.74	0.57	454	0.51	0.97	1.89
379	2.50	2.74	0.43	455	0.49	0.94	1.75
380	2.48	2.74	0.59	456	0.48	0.92	1.78
381	2.46	2.74	1.04	457	0.47	0.90	1.79
382	2.45	2.74	1.06	458	0.45	0.87	1.84
383	2.43	2.74	1.58	459	0.44	0.85	1.80
384	2.41	2.74	2.23	460	0.42	0.82	1.78
385	2.38	2.74	2.16	461	0.41	0.80	1.77
386	2.36	2.73	1.59	462	0.39	0.77	1.70
387	2.34	2.73	0.74	463	0.38	0.75	1.84
388	2.32	2.73	1.38	464	0.37	0.72	1.75
389	2.30	2.72	1.58	465	0.36	0.70	1.84
390	2.27	2.71	1.70	466	0.34	0.68	1.78
391	2.25	2.71	2.11	467	0.33	0.66	1.78
392	2.22	2.70	2.45	468	0.32	0.64	1.65
393	2.19	2.69	2.91	469	0.31	0.62	1.74
394	2.16	2.68	5.53	470	0.30	0.60	1.74
395	2.14	2.66	6.90	471	0.29	0.58	1.69
396	2.11	2.65	9.17	472	0.28	0.56	1.80
397	2.08	2.64	11.65	473	0.27	0.54	1.67
398	2.05	2.62	14.77	474	0.26	0.52	1.77
399	2.02	2.61	25.67	475	0.25	0.51	1.63
400	1.99	2.59	28.78	476	0.24	0.49	1.61
401	1.96	2.56	44.73	477	0.23	0.47	1.73
402	1.93	2.55	60.73	478	0.23	0.46	1.70
403	1.90	2.53	80.00	479	0.22	0.44	1.73
404	1.87	2.51	120.45	480	0.21	0.42	1.62
405	1.84	2.48	165.19	481	0.20	0.41	1.68
406	1.80	2.46	223.60	482	0.19	0.40	1.64
407	1.77	2.44	289.32	483	0.19	0.38	1.76
408	1.74	2.41	423.36	484	0.18	0.37	1.69

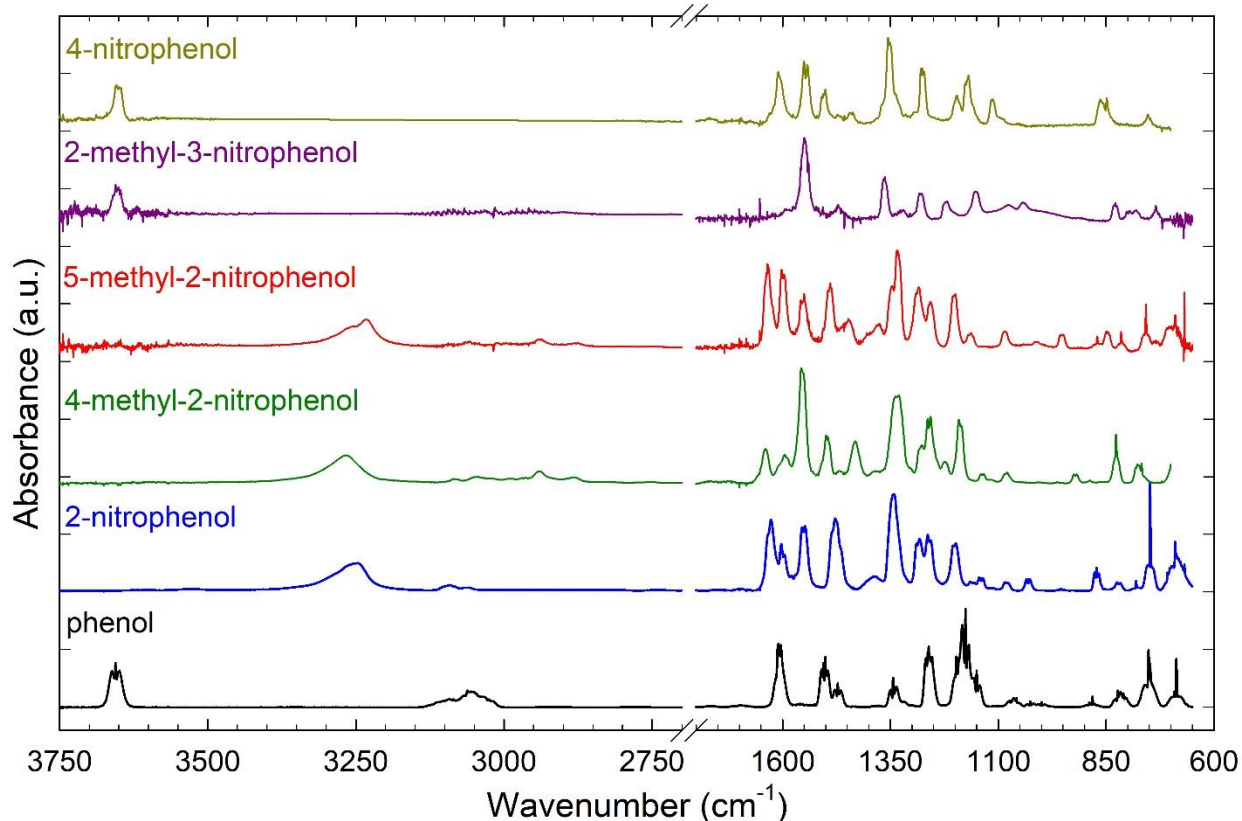
409	1.70	2.39	535.28	485	0.17	0.36	1.77
410	1.67	2.36	681.85	486	0.17	0.34	1.73
411	1.64	2.33	838.44	487	0.16	0.33	1.83
412	1.60	2.30	1090.00	488	0.16	0.32	1.92
413	1.57	2.28	1289.25	489	0.15	0.31	2.42
414	1.54	2.25	1458.40	490	0.14	0.30	3.16
415	1.51	2.22	1754.08	491	0.14	0.28	4.95
416	1.48	2.19	1768.50	492	0.13	0.27	5.23
417	1.45	2.16	1781.33	493	0.13	0.26	3.52
418	1.41	2.13	1876.48	494	0.12	0.25	2.41
419	1.38	2.10	1809.75	495	0.12	0.24	1.90
420	1.35	2.07	1767.25	496	0.11	0.23	1.76
421	1.32	2.03	1712.93	497	0.11	0.23	1.61
422	1.28	2.00	1680.45	498	0.11	0.22	1.61
423	1.25	1.97	1556.10	499	0.10	0.21	1.64
424	1.22	1.93	1439.23	500	0.10	0.20	1.66
425	1.19	1.90	1358.03				

In an attempt to preliminary evaluate the gas-phase products formed from the photolysis and from the OH radical initiated gas-phase oxidation of nitrocatechols, the infrared spectra for these reactions were evaluated. No ring-retaining or ring-opening products were identified from the photolysis or photooxidation of the investigated nitrocatechols. However, the residual photolysis product spectra illustrated in **Figure S4** show clear absorption features at  $2139\text{ cm}^{-1}$  for 3NCAT and  $2135\text{ cm}^{-1}$  for 5M3NCAT. The photolysis mechanism of nitroaromatic compounds leading to the formation of a ketene-type product and HONO elimination has been previously proposed (Bejan et al., 2020), similar to the carboxylic acid formation mechanism in aqueous phase proposed by Alif et al. (1991).



**Figure S4:** Residual spectra from the gas-phase photolysis of (A) 3NCAT and (B) 5M3NCAT at 365 nm.

Additionally, the intramolecular H-bond formed between the phenolic H and O-atom from the nitro group can be observed by investigating the gas-phase IR spectra of 2-, 3-, and 4-nitrophenols presented in **Figure S5**. Bejan (2006) has presented similar findings for 2-nitrophenol in comparison with 3- and 4-nitrophenol isomers. **Figure S5** adds even more spectral evidence with the main aim to highlight the differences between the OH band position in the gas-phase IR spectra of phenol, 2-methyl-3-nitrophenol and 4-nitrophenol with those from 2-nitrophenols. Spectral shifts up to  $350\text{ cm}^{-1}$  were observed between the OH band positions.



**Figure S5:** Gas-phase IR spectra of phenol, several 2-nitrophenols, 2-methyl-3-nitrophenol and 4-nitrophenol.

The substituents interactions and their influence in the gas-phase OH-reactivity of nitrocatechols and nitrophenols were extensively discussed in the manuscript. Additionally, **Table S2** presents the updated values of Kwok and Atkinson (1995) SAR method with respect to the electrophilic substituents  $\sigma_i^+$  contribution used in estimation of the kOH addition pathway and considerations given in other investigations (Brown and Okamoto, 1958; Zetzsch, 1982; Rinke and Zetzsch, 1984). In the case of 3-nitrocatechol and 5-methyl-3-nitrocatechol, the value with the most negative  $\Sigma\sigma_i^+$  corresponds to *o*- and *p*- positions relative to the NO<sub>2</sub> substituent group. This is attributed to the fact that the OH placed next to the NO<sub>2</sub> could not influence the addition pathway since its shielding prevails. Very good estimated rate values are obtained in using this attempt for 3NCAT, 5M3NCAT and 4M5NCAT. However, for 4NCAT and nitrophenols this updated estimation tends to under evaluate the experimental data. Unfortunately, given the fact that in the catechol structure, the second OH group has no contribution to the addition pathway, the  $\sigma^+$  for *meta* and/or *ipso* positions being neglected, no relevant new updated values could be now performed for  $\sigma^+$  for the lone-pair NO<sub>2</sub> substituents.

**Table S2:** Rate coefficients for the reaction of nitroaromatic compounds with OH radicals at room temperature calculated from Kwok and Atkinson (1995) SAR updated for the internal effects observed in nitrophenols and nitrocatechols, along with the electrophilic substituents constants proposed by Brown and Okamoto (1958) and Zetzsch (1982).

Compound	$\sigma_i^+$	$\Sigma\sigma_i^+$	$k_{abs}\times 10^{13}$	$k\times 10^{12}$ ( $\text{cm}^3 \times \text{s}^{-1}$ )
Nitrobenzene	0.674 [m-(NO <sub>2</sub> )]	0.674	-	0.244
m-nitrotoluene	-0.311 [p-(CH <sub>3</sub> )] 0.79 [p-(NO <sub>2</sub> )]	0.479	1.36 (CH <sub>3</sub> )	0.581
2-nitrophenol	0.674 [m-(NO <sub>2</sub> )]	0.674	-	0.244
3-methyl-2-nitrophenol	-0.311 [p-(CH <sub>3</sub> )] 0.674 [m-(NO <sub>2</sub> )]	0.363	1.36 (CH <sub>3</sub> )	0.772
5-methyl-2-nitrophenol	-0.311 [p-(CH <sub>3</sub> )] 0.674 [m-(NO <sub>2</sub> )]	0.363	1.36 (CH <sub>3</sub> )	0.772
4-methyl-2-nitrophenol	-0.311 [p-(CH <sub>3</sub> )] 0.79 [p-(NO <sub>2</sub> )]	0.479	1.36 (CH <sub>3</sub> )	0.581
6-methyl-2-nitrophenol	-0.311 [p-(CH <sub>3</sub> )] 0.79 [p-(NO <sub>2</sub> )]	0.479	1.36 (CH <sub>3</sub> )	0.581
3-nitrocatechol	-0.92 [o-(OH)] 0.79 [p-(NO <sub>2</sub> )]	-0.130	1.4 (OH)	3.052
4-nitrocatechol	0.674 [m-(NO <sub>2</sub> )]	0.674	1.4 (OH)	0.384
5-methyl-3-nitrocatechol	-0.92 [o-(OH)] -0.311 [p-(CH <sub>3</sub> )] 0.79 [p-(NO <sub>2</sub> )]	-0.441	1.4 (OH) 1.36 (CH <sub>3</sub> )	7.878
4-methyl-5-nitrocatechol	-0.311 [p-(CH <sub>3</sub> )] 0.674 [m-(NO <sub>2</sub> )]	0.363	1.4 (OH) 1.36 (CH <sub>3</sub> )	0.912

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