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### COMMUNICATION

# Reversible Regulating of Crystal Structures Based on Isomerization of Phenylhydrazones

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Reversible crystal transformation for phenylhydrazones 1 between the orthorhombic microporous 1-*E* crystal and monoclinic herringbone 1-*Z* crystal induced by light and heating has been demonstrated. Other than the inherent single-molecular photoreactivity, the weak intermolecular interactions and loose stacking of porous 1-*E* crystal favor the efficient solid-state photoisomerization.

The development of novel optically switchable solid materials is of great interest for separation, catalysis, photomechanical actuation and particularly the energy conversion and storage. Photochromic molecules capable of undergoing reversible structural interconversion by light radiation are promising building blocks for the implementation of photoswithable functions within supramolecular species and bulk solid materials.<sup>1</sup> However, most photochromic compounds in solid state show suppressed photoreactivity due to the close stacking by hydrogen bonds,  $\pi$ - $\pi$  coupling or other intermolecular interactions. In addition, some molecules suffer the photo-damage upon light stimuli, which severely limits the photo-responsive performance in solid state.<sup>2</sup> Construction of photoactive solid materials with photoresponsive behavior, especially the reversible photoswitchable properties, is still a challenge to date. Great efforts have been made on this issue mainly in two aspects: a) optimization of the photochromic molecular building blocks with high photoisomerization yield, good stability, excellent cyclic reversibility and fatigue resistance to ensure the inherent single-molecular photoreactivity; b) organization of these photoreactive molecules by controlled assembly into orderly and loose stacking superstructures, such as the porous molecular crystals. The loose stacking endows the molecules in the solid state enough space and freedom for photoisomerization via rotation or inversion mechanism.<sup>3</sup> The single-molecular photochemical events at the microscopic scale thus can be amplified or synchronized by the regular loose arrangement, showing observable changes at some macroscopic scale.<sup>2</sup> Therefore, the construction of the porous molecular crystal with photoresponsive performance via loose stacking of photochromic molecules, is an effective way to achieve the photoswitchable crystalline materials. The porous molecular crystals assembled by intermolecular weak interactions may show substantial advantages in terms of preparation, processability, structural diversification and functional flexibility in comparison with the porous metal-organic and covalent frameworks<sup>4</sup> based on covalent bonds. In addition, crystalline phase transformation based the on photoisomerization converts the photon absorption into the chemical energy and stores it in the metastable crystal then release the stored energy as heat, therefore, the novel photoactive molecular crystals with structural flexibility and photoswitchable performance show potential applications in energy conversion and storage such as the solar thermal cells (STCs). <sup>5</sup> While a few types of compounds with E/Z photoisomerization properties for STCs have been reported, most of which are azobenzene derivatives fabricated in polymer flims.<sup>5b,c</sup> It has been indicated that the phase change between the crystalline solid and the amorphous solid/liquid could be a parameter for designing high energy density photon energy storage materials.<sup>5b</sup> Accordingly, development of novel optically switchable crystalline materials to realize energy storage via crystal transformation is highly interest for energy storage and conversion materials.

Hydrazones<sup>6</sup> that can undergo light and thermal E/Z isomerization around the imine C=N bond are potentially promising photochromic molecules for their higher photoisomerization quantum yield compared with azobenzenes,<sup>3a</sup> and good thermal stability of the Z isomers.<sup>4</sup> Most studies on hydrazones by far are focused on the pH activated isomerization in solution,<sup>6b, 8</sup> and a few examples have been reported on photoisomerization in solution<sup>7,9</sup> but barely in solid state. Herein, we have synthesized phenylhydrazones 1 (Fig. 1a) to construct photoswitchable molecular crystals. The reversible photoisomerization of 1 in solution has been studied in detail. By slow liquid-phase diffusion method, the single crystals of both 1-E and 1-Z

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Electronic Supplementary Information (ESI) available: Experimental details, Scheme S1, Tables S1–S2, and Figures S1–S4 (PDF), Data for **1-***E* and **1-***Z* crystals (CIFs). See DOI: 10.1039/x0xx00000x

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isomers that are hardly achieved have been obtained respectively. Furthermore, the crystal of **1-***E* exhibits regular quasi-hexagonal extrinsic micropores,<sup>10</sup> which is challenging to construct. The porous crystal structure of **1-***E* with the inner free volume and weak intermolecular interactions facilitates the photoswitching of the hydrazones in solid state. Finally, efficient reversible isomerization in the crystalline state was realized with considerable energy conversion between the porous structure of **1-***E* and close herringbone stacking of **1-***Z* isomers under light or heating. The structural flexibility, porosity and versatility of the novel photoswitchable material with substantial energy changed may have promising applications in energy harvesting and storage.



**Fig. 1.** (a) ORTEP drawing of phenylhydrazone **1-***E* (red dotted line: intramolecular hydrogen bond, rose-carmine circle: intramolecular six-member ring) and **1-***Z*; (b) *E*/*Z* isomerization and possible mechanism of phenylhydrazone **1**; (c) UV/vis absorption spectral changes upon the photoisomerization of **1** in THF (0.07 mM). Absorption spectra of **1** before (black trace, mainly **1-***E*) and after (red trace, photostationary state of mainly **1-***Z*) irradiation by 380 nm light for 60s; the grey traces show the evolution of the spectrum with irradiation for t=1, 2, 5, 9, 20, 27, 35, 45 s and the blue trace is the spectrum obtained after stored in the dark for 12 hours at room temperature. (d) Absorbance changes of **1** in THF solution (0.07 mM) measured at  $\lambda$ =376 nm by alternating irradiation by 380 nm light for 60 s and under dark for 12 hours in repeated switching cycles.

Phenylhydrazones **1** with pyridine unit (**Fig. 1a**) were synthesized with the E/Z ratio of about 3:2 (**Scheme S1** and **Fig. S1** in ESI<sup>+</sup>).<sup>2a, 11</sup> The isomerization mechanism<sup>3b</sup> of such hydrazone molecular switches typically involves the changes of the intramolecular hydrogen-bondings, namely the hydrazone-azobenzene tautomerization, followed by rotation around a C-N single bond (**Fig. 1b**).

The photoisomerization of the freshly purified phenylhydrazones 1-E in THF were characterized by UV-vis spectroscopy (Fig. 1c and 1d). The absorption band centered at  $\lambda_{max}$ =376 nm of 1-*E* (Fig. 1c: black line) is assigned to the  $\pi$ - $\pi^*$ transition of the aromatic units, which can weaken the C=N bond and facilitate the E/Z isomerization.<sup>7, 12</sup> Irradiation of the 1-E solution with light of 380 nm results in blue shift of the absorption band, reaching the photostationary state (PSS) at  $\lambda_{max}$ =370 nm after 60 seconds (red line), leading to the formation of 1-Z isomers with the estimated yield of about 95% (Part 3 in ESI<sup>†</sup>).<sup>12</sup> Putting this reaction mixture in dark for 12 hours at room temperature, the absorption spectra reverted back to the original state, which indicates the reversible isomerization from 1-Z to 1-E isomers. The isosbestic points ( $\lambda$ =370 and 310 nm) demonstrate that only two species (1-E and 1-Z isomers) are involved during the isomerization process.<sup>2a</sup> Furthermore, no obvious photodegradation occurred during multiple isomerization cycles of the system ( $\geq$ 

10 times, **Fig. 1d**), showing good reversibility and photochemical fatigue resistance of phenylhydrazones **1**.



**Fig. 2.** (a) Molecular packing of **1**-*E* crystal viewed along *c* axis with porous fluctuated hexagonal pattern composed of four kinds of dimers (A, B, C, D) with each pore diameter of about 7.07 Å; (b) Molecular packing of **1**-*E* crystal viewed along *b* axis; (c) Molecular packing of **1**-*E* crystal viewed along *c* axis by the spacefill style; (d) Molecular packing of **1**-*Z* crystal viewed along *c* axis with four molecules (A, B, C, D); (e) Molecular packing of **1**-*Z* crystal viewed along *c* axis with staggered herringbone mode.

The single crystals of 1-E and 1-Z isomers were obtained respectively by slow liquid-phase diffusion method (Table S1). As far as we know, this is the first report on the crystal of the Z-isomer that was finely growth from solution. In the 1-E crystal, an intramolecular hydrogen bond is formed in each Eisomer between the pyridine nitrogen and the hydrogen on the hydrazone, leading to the formation of a six-member ring (Fig. 1a, rose-carmine circle), which is somewhat twisted but rigid that may prevent a tight stacking  $^{\rm 13}$  between the molecules. The crystal here has indicated that such loose stacking can lead to a porous structure, which is believed to be a key factor to achieve the switchable performance in solid state.<sup>14</sup> On account of the twisting of the H-bonded rings, two molecules packed into a dimmer in slightly slipped arrangement with rotation angle of about 121.6° and  $\pi$ - $\pi$ stacking distance of 3.24 Å (Fig. 2b) by four distinctive patterns (Fig. 2a: A, B, C and D) to form one unit cell. The unit cell composed of four different dimmers forms in the on-top "Zigzag" mode at ab plane (Fig. 2a, 2c) and then crystallizes in an orthorhombic space group Pccn. Consequently, two quasihexagonal pore I and pore II (Fig. 2a) are constructed by the zigzag packing with six dimmers of A1, B1, C1, B2, A2, D3 and C1, D1, A4, D2, C2, B2 respectively. The pores II and pores I stacked up and down along a axis to form the fluctuated arrangement (Fig. 2b and 2c) with uniform minimum diameter of about 7.07 Å.<sup>15</sup> Overall, extrinsic micropores are formed with fluctuated quasi-hexagonal channels along c axis (Fig. 2b and **2c**) with a porosity of about 17% calculated by Platon.<sup>1</sup>

In the **1-Z** crystal, only the **Z**-configuration molecules are observed, which shows increased planarity without intramolecular hydrogen bonds (**Fig. 1a**). The **1-Z** isomers crystallize in the monoclinic space group P 21/n with the unit cell composed by four molecules A, B, C and D in the on-top "line" mode at *ac* plane (**Fig. 2d**) with intermolecular H-bonds (2.31 Å) and C-H···N interactions (2.73 Å and 2.64 Å) between each two molecules (B and C, A and D' or D and A", **Fig. S2** in ESI<sup>†</sup>), which further enhance the stability of **Z**-isomers in solid. The four molecules stacked alternately in staggered forward and reverse herringbone modes at *ab* plane (**Fig. 2e**). Two neighboring molecules are oriented in a face-to-face staking to form columns along *b* axis by the  $\pi$ - $\pi$  interactions with shorter distance of 3.18 Å (**Fig. 2e**). In brief, the **1-Z** isomers bearing

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planar structure stack densely into herringbone arrangement with no porosity in the crystal.

Comparing the molecular structures of the two isomers 1-E and 1-Z, and the corresponding crystalline structures, one may figure out the decisive role of the intramolecular H-bonds in controlling the crystal structure. The intramolecular H-bonds formed in the 1-E isomers induced strong tension within the molecule (Fig. 1a), leading to the increased rigidity and distortion of the molecule structure, therefore weaken the  $\pi$ - $\pi$ interaction by enlargement of the  $\pi$ - $\pi$  distance (3.24 Å). By virtue of the solely weak  $\pi$ -interaction along the *c* axis, the **1-***E* isomers stack loosely to form porous crystalline structure.<sup>17</sup> In the case of the 1-Z isomers, intramolecular H-bonding is infeasible because of the Z-configuration and the far distance between the nitrogen of cyano group and the hydrogen on hydrazone, which leaves the planar molecular structure that favors the close face-to-face  $\pi$ - $\pi$  stacking<sup>18</sup> with shorter distance of 3.18 Å along the b axis. In addition, other intermolecular interactions, such as the intermolecular Hbonds and C-H...N interactions along a and c axis, are demonstrated (Fig. S2), which coherently construct the 1-Z crystal with tight herringbone arrangement. Considering the multiple intermolecular interactions and the compact molecular stacking within the 1-Z crystal but the exclusive and weak  $\pi$ -stacking in the **1-***E* crystal, efficient transformation between the 1-E and 1-Z crystals are expected, which will be verified by the UV-visible absorption spectroscopy and X-ray powder diffraction (XRPD) as illucidated vide infra. Therefore, appropriate increase in the rigidity and distortion of the molecular structures by intramolecular H-bonding may weaken and reduce the intermolecular interactions to prevent the close stacking, and therefore is benefit for the formation of porous material.



**Fig. 3.** Observation of the photoisomerization of **1-E** in a drop-cast thin film by UV-visible absorption spectroscopy and X-ray powder diffraction (XRPD): (a) Absorption spectra of **1-E** film before (I) and after (II) irradiation at 475 nm for 22 h; Curve III is the spectrum obtained when annealed at 76 °C under vacuum for 10 min. Spectra taken at different irradiation times of 2, 5, 16 and 22 h are shown in grey lines; (b) XRPD patterns obtained before (II) and after 22 h (III) irradiation the film of **1-E** at 475 nm. Curve I and V are patterns calculated from single-crystal data of **1-F** and **1-Z**. Curve IV is the pattern obtained by annealing of the irradiated film at 76 °C under vacuum for 10 min.

The solid-state photoreactivity of **1** was checked on the **1-***E* drop-cast thin films by tracking the UV-visible absorption changes with light or heat stimuli. The maximum absorption centered at  $\lambda_{max} = 475$  nm of **1-***E* (Fig. **3a**: Curve I, black) film shows substantial (~100 nm) red-shift compared with the absorption of individual molecules in solution (Fig. **1c**: black trace). This clearly suggests the *J*-aggregation<sup>19</sup> and conforms to the slipped rotating arrangement between the two molecules within a starting dimer of the **1-***E* crystal (Fig. **2a**). Irradiation of the **1-***E* film with the light of 475 nm brings about an obvious blue-shift of about 22 nm (Fig. **3a**: Curve II, red), indicating the efficient *E*→*Z* photoisomerization in solid state wtih about 91% of the **1-***Z* isomers<sup>12</sup> obtained at the PSS. After

annealing the irradiated film at 76°C under vacuum for 10 min, the absorption spectra converted back almost completely (Fig. **3a**: Curve III, blue), which indicated the  $Z \rightarrow E$  isomerization. The above shows that **1-***E* is the thermodynamically stable form in solid state and the photoreaction is a nearly absolute process.

To get deep insight into the isomerism in solid state, the Xray powder diffraction (XRPD) of the drop-cast film of 1-E were performed by light irradiation or heat treatment. The XRPD pattern obtained from the films of 1-E (Fig. 3b: Curve II, red) is almost identical to the pattern calculated from single-crystal data (Fig. 3b: Curve I, black), indicating the film structure is resemble to that of the crystalline particles. The diffraction peak at  $2\theta$ =7.18° in curve II can be ascribed to the refractions from two dimmers side by side (A and B or C and D ) in the unit cell of crystal 1-E (Fig. 2a). The corresponding d spacing is 12.3 Å with the miller index (110) (Table S2), representing the length of the two dimmers (Fig. 4) according to the calculated crystal morphology from the BFDH model <sup>20</sup> (Fig. S3). The diffraction peak at  $2\theta$ =7.89° with the miller index (200) and d spacing of 11.2 Å (Table S2) which is a half of the axial length of *a* axis in the unit cell, can be ascribed to the width of the corresponding two dimmers (Fig. 4 and Fig. S3). After 22 h irradiation of the film by light of 475 nm, the peaks belonging to the 1-E crystal disappeared, accompany with new peaks emerged at 7.50° and 15.0° as shown in Fig. 3b (Curve III, blue). According to the mentioned E to Z photoisomerization occurred upon 475 nm light irradiation, this photo-induced PXRD pattern should be corresponding to the generation of 1-Z isomers, which may be the indication of the phase transition from the porous orthorhombic syngony of 1-E to the herringbone monoclinic syngony of **1-Z**. The corresponding d spacing of the emerging peaks are 11.8 Å with the miller index (10-1) and the secondary diffraction of 5.91 Å with the miller index (20-2) (Table S2), respectively, which are well coincide with the length of one molecule in the unit cell of crystal 1-Z (Fig. 4 and Fig. S3). Notably, the XRPD signals of the 1-E crystals are almost recovered upon annealing the irradiated film at 76 °C under vacuum for 10 min (Fig. 3b: Curve IV, green), suggesting the restoring porous orthorhombic crystalline phase upon heating. The above results are clearly evident that the crystal structure change is reversible and correlated to the E/Z interconversion.



Fig. 4. Schematic illustration of the phase transition process between the porous orthorhombic crystal of 1-*E* and the herringbone monoclinic crystal of 1-*Z* by light or heating.

A rational phase transition mechanism is proposed as shown in **Fig. 4**, including the following steps: (1) when irradiation of the porous crystal of 1-E at 475 nm, photoisomerization

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occurred on the molecular level, where the **1-***E* isomer transforms into the **1-***Z* configuration accompany with the intramolecular H-bond broken; (2) the slightly slipped molecular stacking with large rotation angle of about 121.6° in each dimer changes into the face-to-face  $\pi$ - $\pi$  stacking without rotation; (3) four dimers in the on-top "Zigzag" mode as one structure repeating unit of the **1-***E* crystal rearrange into an on-top "line" mode serving as two building blocks to the **1-***Z* crystal, and (4) the on-top "line" mode building blocks arrange along *a* and *c* axis to form into the herringbone structure of **1-***Z* crystal. The phase transition from 1-*Z* to 1-*E* crystal promoted by heating occurs by the reverse process.

The efficient photoisomerization was realized in hydrazones crystals, relying on the solely weak intermolecular interactions and loose packing between the molecules in the porous 1-E crystal, beyond the inherent good single-molecular photoreactivity of the molecules. To the best of our knowledge, substantial  $E \rightarrow Z$  photoisomerization of hydrazone between two crystalline phases is described for the first time, and on consideration of such crystalline structure transformation, effective enthalpy change desired for the energy storage is expected. Accordingly, the enthalpy change ( $\Delta H$ ) from the metastable 1-Z to thermodynamically stable 1-E in solid states was checked by differential scanning calorimetry and thermogravimetric analysis (DSC-TG) on the 1-Z polycrystalline powders. The DSC-TG curves (Fig. S4) indicate the 1-Z to 1-E thermal isomerization occurs during the melting of the 1-Z polycrystalline powders with a enthalpy change of 32.3 kJ/mol, which is comparable to the azobenzene in condensed phase,<sup>5b,c</sup> showing potential application in energy harvesting and storage. This value is much higher than the photoisomerizatin induced enthalpy change from 1-Z to 1-E at moleluar level (18.4 kcal/mol) as estimited by the density functional theory (Table S3), <sup>21</sup> suggesting the large contribution on the energy change from the multiintermolecular interections as mentioned above.

In conclusion, the reversible photoisomerization of phenylhydrazones 1 in solution and the crystalline state has been well demonstrated. Upon irradiation of 380 nm light or stored in dark, the cyclic single-molecular photoisomerizations between 1-E and 1-Z isomers in THF show good reversibility and photochemical fatigue resistance. Above all, such photoisomerization could proceed in crystalline state, which induced identified crystalline structures of the 1-E and 1-Z isomers. The intramolecular hydrogen bonds in the 1-E molecules lead to the distortion and rigidity of the molecular structures, which prevent a close-packed arrangement in the crystals and promote low-density molecular self-assembly, affording porous molecular crystals with fluctuated quasihexagonal channels of about 7.07 Å in diameter and a porosity of about 17%. This relatively loose stacking facilitates the  $E \rightarrow Z$ photoisomerization in the solid state. The efficient bulk photoisomerization induces the disappearance of the pore structure from the porous (1-E) to herringbone (1-Z) crystalline structure. The micropores can also be restored upon  $Z \rightarrow E$ isomerization promoted by heating with the enthalpy ( $\Delta H$ ) of 32.3 kJ/mol in melting state following the reverse process. The structural flexibility and photoswitchable performance make this novel photoactive material interesting in energy harvesting, storage and conversion. It also paves the way to a better understanding of solid-state photochemical reactions and photoinduced crystalline phase transitions. The special combination of porosity and novel photoactive moieties opens up intriguing perspectives in the field of photoresponsive materials.

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There are no conflicts to declare.

#### Notes and references

**‡** Details of the synthesis and structural characterization are provided in ESI**†** (Scheme S1 and Figure S1). CCDC numbers of the single crystals: 1486572 for 1-*E*, 1486571 for 1-*Z*.

- 1 S. Kobatake, M. Irie, et al. *Nature* 2007, **446**, 778-781.
- 2 a) Y. Yang, I. Aprahamian, et al. J. Am. Chem. Soc. 2012, 134, 15221–15224; c) X. Yao, H. Tian, et al. Adv. Opt. Mater. 2016, 4, 1322-1349.
- 3 a) H. M. D. Bandara, S. C. Burdette, *Chem. Soc. Rev.* 2012, 41, 1809-1825; b) S. M. Landge, E. Tkatchouk, W. A. Goddard, I. Aprahamian, *J. Am. Chem. Soc.* 2011, 133, 9812-9823.
- a) H-C. J. Zhou, S. Kitagawa, Chem. Soc. Rev. 2014, 43, 5415-5418; b) F. X. Coudert, Chem. Mater. 2015, 27, 1905–1916.
- 5 a) T. J. Kucharski, R. Boulatov, et al. Energy Environ. Sci., 2011, 4, 4449; b) G. D. Han, J. C. Grossman, et al. J. Mater. Chem. A 2016, 4, 16157-16165; c) K. Ishiba, C. Chikara, N. Kimizuka, et al. Angew. Chem. Int. Ed., 2015, 54, 1532–1536.
- 6 a) A. C. Pratt, Chem. Soc. Rev. 1977, 6, 63-81; b) L. A. Tatum, I. Aprahamian, Acc. Chem. Res. 2014, 47, 2141-2149.
- 7 a) D. G. Belov, S. M. Aldoshin, et al. *Russ. Chem. Bull.* 2000,
  49, 666-668; b) M. N. Chaur, D. Collado, J. M. Lehn, *Chem. Eur. J.* 2011, 17, 248-258.
- 8 a) X. Su, T. F. Robbins, I. Aprahamian. Angew. Chem. Int. Ed. 2011, **50**, 1841-1844; b) I. Aprahamian, Nat. Chem. 2016, **8**, 97-99.
- 9 S. Yamamura, K. Ichimura, et al. *Chem. Lett.* 1992, **21**, 543-456.
- 10 a) J. R. Holst, A. Trewin, A. I. Cooper, Nature Chem. 2010, 2, 915–920; b) J. Li, R. Cao, Angew. Chem. Int. Ed. 2016, 55, 9474-9480.
- 11 P. Cankař, J. Slouka, et al. J. Heterocycl. Chem., 2003, 40, 71-76.
- 12 K. Stranius, K. Börjesson, Sci. Rep. 2017, DOI: 10.1038/ srep41145.
- 13 a) A. Isabelle, R. Odile, et al. J. Am. Chem. Soc. 2001, **123**, 8177–8188; b) S. Hong, K. Kim, et al. Angew. Chem. Int. Ed. 2015, **54**, 13241-13244.
- 14 M. Baroncini, A. Credi, et al. *Nat. Chem.* 2015, **7**, 634-640.
- 15 M. Mastalerz, I. M. Oppel, Angew. Chem. Int. Ed. 2012, **51**, 5252-5255.
- 16 a) P. Van der Sluis, A. L. Spek, Acta Crystallogr. Sect. A 1990,
  46, 194; b) A. L. Spek, Acta Crystallogr. Sect. D 2009, 65, 148.
- 17 Y. Liu, W. Gan, et al. Liq. Cryst. 2011, 38, 995-1006.
- 18 L. Yuan, Z. Wei, et al. Adv. Mater. 2016, 28, 5980-5985.
- 19 a) K. Ariga, T. Kunitake, et al. J. Am. Chem. Soc. 1997, **119**, 2224-2231; b) F. Wang, K. Hashimoto , K. Tajima, Adv. Mater. 2015, **27**, 6014-6020.
- 20 a) E. Moreno-Calvo, et al. Cryst. Growth Des., 2010, 10, 4262-4271; b) V. Lloveras, J. et al. Chem. Eur. J. 2016, 22, 1805-1815.
- 21 a) M. J. Frisch, et al. Gaussian 03, revision B.05, Gaussian, Inc., 2003; b) C. T. Lee, R. G. Parr, Phys. Rev. B 1988, 37, 785–789; c) M. M. Francl, J. A. Pople, et al. J. Chem. Phys. 1982, 77, 3654–3665.

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