

# Partition of the Dipole Moment and Atomic Polar Tensor: The Water Molecule

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A partition of the atomic polar tensor (APT) into charge, charge flux, and atomic and homopolar dipole fluxes is proposed by analyzing the variations of the dipole moment vector with respect to the expectation integrals of the atomic basis functions. The contributions in the expression obtained for the dipole moment are invariant with respect to the origin of the system and contain the atomic and homopolar dipoles as named before by Mulliken and Coulson. Results for water molecule are presented as an illustration of the method.

## Dipole Moment Partitioning

Although the dipole moment  $\mathbf{p} = (p_x, p_y, p_z)^T$  of a neutral molecule is invariant with respect to the origin to which it has been calculated, the magnitude of its contributions is sensitive to the choice of origin. A previous partition of the dipole moment vector, invariant with respect to the origin, has been proposed by Ruedenberg<sup>1</sup> for valence atomic orbitals for which all the intraatomic off-diagonal bond order matrix elements are null.

The expectation value for the  $p_x$  component of the dipole moment operator for an  $N$ -electron molecule in the atomic system of units is given by

$$\langle \hat{p}_x \rangle = \langle \Psi_0 | \hat{p}_x | \Psi_0 \rangle = - \sum_{i=1}^N \langle \Psi_0 | x_i | \Psi_0 \rangle + \sum_A Z_A X_A \quad (1)$$

where  $x_i$  and  $X_A$  are the electron and nuclear coordinates respectively, and  $Z_A$  is the charge of nucleus A.

For a closed-shell molecule described by a single determinant wave function,  $|\Psi_0\rangle = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \dots \psi_{N/2} \bar{\psi}_{N/2}\rangle$ , we have

$$\langle \hat{p}_x \rangle = -2 \sum_{i=1}^{N/2} \langle \psi_i | x_i | \psi_i \rangle + \sum_A Z_A X_A \quad (2)$$

In the LCAO approximation, the molecular orbitals are  $\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}$  and the dipole moment

$$\langle \hat{p}_x \rangle = - \sum_{\mu} \sum_{\nu} P_{\mu\nu} \langle \phi_{\mu} | x | \phi_{\nu} \rangle + \sum_A Z_A X_A \quad (3)$$

where  $P_{\mu\nu}$  is the density matrix element, given by

$$P_{\mu\nu} = 2 \sum_i^{N/2} C_{\mu i}^* C_{\nu i}$$

In eq 3, the dipole moment is given by two contributions, the first, a quantum mechanical contribution of the electrons, and, the second, a classical contribution of the nuclei. These two contributions change as the origin is changed. Rearranging the electronic contribution results in

$$- \sum_{\mu} \sum_{\nu} P_{\mu\nu} \langle \phi_{\mu} | x | \phi_{\mu} \rangle - \sum_{\mu} \sum_{\nu} 2P_{\mu\nu} \langle \phi_{\mu} | x | \phi_{\nu} \rangle - \sum_{A < B} \sum_{\mu} \sum_{\nu} 2P_{\mu\nu} \langle \phi_{\mu} | x | \phi_{\nu} \rangle \quad (4)$$

where the upper indices on the summation signs mean that  $\mu$  belongs to A and  $\nu$  to B. The first two terms in the above equation refer to atomic contributions and the integrals give the expectation values of the centers of electronic charges while the last term is related to all the chemical bonding in the molecule. Assuming that the basis functions are centered on the nuclei, the expectation values of the first term are at the corresponding nuclei, and  $\langle \phi_{\mu} | x | \phi_{\mu} \rangle = X_A$ . The integrals of the second term result from the hybridization of the  $\mu$  and  $\nu$  atomic orbitals. The center of electronic charge in this case is not usually on the nucleus since the hybrid orbital no longer has central symmetry.  $P_{\mu\nu}$  in the third term is related to the charge density between two atoms, and the

TABLE I: Dipole Moment Partitioning (bohr-e) for H<sub>2</sub>O Molecule<sup>a</sup>

basis funcn	$\sum q_A R_A$	at. dipole	homopolar dipole		$p_z$
			OH	HH	
STO-6G	-0.4245	-0.7751	0.2534	0.0	-0.693
4-31G	-0.8692	-0.7278	0.2854	0.0	-1.026
					-0.723 <sup>b</sup>

<sup>a</sup> Molecule in the YZ plane; the negative Z axis bisects the HOH angle. Bond length = 1.809 au and bond angle = 104.52°.

<sup>b</sup> Experimental value.

integrals give the center of charge of the bonding electrons.

Concerning the nuclear contribution, the nuclear charge  $Z_A$  can be written as  $Z_A = q_A + Q_A$ , where  $q_A$  and  $Q_A$  account for the Mulliken net and gross atomic charge.<sup>2</sup> According to the Mulliken population analysis, the nuclear charge for A can be written as

$$Z_A = q_A + \sum_{\mu} P_{\mu\mu} S_{\mu\mu} + \sum_{\mu < \nu} 2P_{\mu\nu} S_{\mu\nu} + \frac{1}{2} \sum_{B \neq A} \sum_{\mu} \sum_{\nu} 2P_{\mu\nu} S_{\mu\nu} \quad (5)$$

which upon substitution in the dipole moment expression yields

$$\langle \hat{p}_x \rangle = - \sum_{\mu} \sum_{\nu} P_{\mu\nu} X_A - \sum_{\mu} \sum_{\nu} 2P_{\mu\nu} \langle \phi_{\mu} | x | \phi_{\nu} \rangle - \sum_{A < B} \sum_{\mu} \sum_{\nu} 2P_{\mu\nu} \langle \phi_{\mu} | x | \phi_{\nu} \rangle + \sum_A q_A X_A + \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} X_A + \sum_{\mu < \nu} \sum_{A \neq B} \sum_{\mu} \sum_{\nu} 2P_{\mu\nu} S_{\mu\nu} X_A \quad (6)$$

Note that  $S_{\mu\nu} X_A = \langle \phi_{\mu} | X_A | \phi_{\nu} \rangle$  and  $S_{\mu\mu} = 1$  so that

$$\langle \hat{p}_x \rangle = + \sum_A q_A X_A - \sum_{\mu} \sum_{\nu} 2P_{\mu\nu} \bar{x}_{\mu\nu}^A - \sum_{A < B} \sum_{\mu} \sum_{\nu} 2P_{\mu\nu} \bar{x}_{\mu\nu}^{AB} \quad (7)$$

where

$$\bar{x}_{\mu\nu}^A = \langle \phi_{\mu} | x - X_A | \phi_{\nu} \rangle \quad \text{and} \quad \bar{x}_{\mu\nu}^{AB} = \left\langle \phi_{\mu} \left| x - \frac{X_A + X_B}{2} \right| \phi_{\nu} \right\rangle$$

The first two terms in eq 7 are of atomic origin where the first one, involving the net atomic charge, is the only term with a classical counterpart. The second term resembles Coulson's atomic dipole,<sup>3</sup> and the integral  $\bar{x}_{\mu\nu}^A$  is the distance from the centroid of the hybrid orbital to nucleus A. For the third term, the integral  $\bar{x}_{\mu\nu}^{AB}$  is the distance of the center of charge from the midpoint of the chemical bond A-B. This contribution to the dipole moment has been referred to as the homopolar dipole<sup>4</sup> by Mulliken. As can be seen, the dipole moment has been partitioned into three contributions: the net atomic charge, the atomic dipole, and the homopolar dipole. Since the density matrix is invariant with respect to the choice of origin and since the sum of all net atomic charges vanishes, this partitioning of the dipole moment does not depend on the choice of origin for the system.

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## Results

In Table I results calculated by the ab initio SCF method using the STO-6G<sup>5</sup> and 4-31G<sup>6</sup> basis sets and eq 7 for the water molecule are presented. The molecule is in the YZ plane, and the negative Z axis bisects the HOH angle. The only atomic dipole contribution comes from the oxygen atom since it is the only element that has different orbitals on the same atom. In this case, almost all of the atomic dipole comes from the (2s,2p<sub>z</sub>) hybrid orbital, which is mainly associated with one of the lone pairs (−0.7856 and −0.7338 bohr·e for STO-6G and 4-31G basis sets, respectively).

Most of the homopolar dipole contribution to the dipole moment comes from the interaction between the 1s orbitals of the hydrogens and the 2p<sub>z</sub> orbital of the oxygen atom (0.2726 and 0.2562 bohr·e for STO-6G and 4-31G basis sets, respectively). Although the center of the charges for the homopolar dipole is dislocated in the direction of the oxygen atom, the polarity of the O–H bond is not as nearly important in determining the dipole moment value as the lone pair in the atomic dipole (remember that the other lone-pair orbital (2p<sub>x</sub>) does not contribute to the dipole moment). The main difference for the dipole moment contributions considering the two basis sets occurs for the net atomic charge term which is 100% higher for the 4-31G basis set.

## Atomic Polar Tensor Partitioning

One of the most useful methods for interpreting and predicting infrared intensities comes from the atomic polar tensor (APT) formalism.<sup>7</sup> In the APT framework, the derivative of the molecular dipole moment vector with respect to the *i*th normal coordinate (which is directly related to the infrared intensity of the *i*th fundamental mode), can be expressed as

$$\frac{\partial \mathbf{p}}{\partial Q_i} = \sum_{\alpha} \sum_{\xi} \frac{\partial \mathbf{p}}{\partial \xi_{\alpha}} [AU^{-1}L]_{\xi\alpha i} \quad (8)$$

where

$$\mathbf{p} = \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix}$$

For each atom  $\alpha$  in the molecule, the quantities  $\partial p_{\tau} / \partial \xi_{\alpha} = P_{\tau\xi}$ , where  $\tau = x, y, z$  and  $\xi = X, Y, Z$ , form the APT, represented by a  $3 \times 3$  matrix  $\mathbf{P}_x^{(\alpha)}$

$$\mathbf{P}_x^{(\alpha)} = \begin{vmatrix} \partial p_x / \partial X_{\alpha} & \partial p_x / \partial Y_{\alpha} & \partial p_x / \partial Z_{\alpha} \\ \partial p_y / \partial X_{\alpha} & \partial p_y / \partial Y_{\alpha} & \partial p_y / \partial Z_{\alpha} \\ \partial p_z / \partial X_{\alpha} & \partial p_z / \partial Y_{\alpha} & \partial p_z / \partial Z_{\alpha} \end{vmatrix} = \nabla_{\alpha} \mathbf{p} \quad (9)$$

So, if all the experimental infrared intensities and normal coordinates are known as well as the permanent dipole moment for a given molecule, the APT can be determined. On the other hand, these APTs can also be calculated by the SCF method and used to predict infrared intensities. These intensities can then be interpreted by partitioning the APT. This has been done before in the "charge-charge flux-overlap" (CCFO) model, first introduced by King and Mast<sup>8</sup> and later applied by Person et al.<sup>9</sup>

By use of eq 7, a general expression for the APT can be obtained:

$$\nabla_{\alpha} \mathbf{p} = q_{\alpha} \mathbf{E} + \sum_A (\nabla_{\alpha} q_A) \mathbf{R}_A - \sum_{A < \mu < \nu} \nabla (2P_{\mu\nu} \mathbf{R}_{\mu\nu}^A) - \sum_{A < B} \sum_{\mu < \nu} \nabla (2P_{\mu\nu} \mathbf{R}_{\mu\nu}^{AB}) \quad (10)$$

where  $\mathbf{E}$  is the identity matrix and each term of the APT is

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TABLE II: Ab Initio STO-6G and 4-31G APT Partitioning for the H<sub>1</sub><sup>a</sup> Atom of the Water Molecule: Charge, Charge-Flux, and Atomic Dipole Flux Contributions

	STO-6G			4-31G		
charge	0.192	0.0	0.0	0.392	0.0	0.0
	0.0	0.192	0.0	0.0	0.392	0.0
	0.0	0.0	0.192	0.0	0.0	0.392
charge flux	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	-0.240	-0.190	0.0	0.008	0.004
	0.0	-0.180	-0.213	0.0	0.095	-0.051
$-\sum_{A < \mu < \nu} \sum^A 2(\nabla_{\alpha} P_{\mu\nu}) \mathbf{R}_{\mu\nu}^A$	0.350	0.0	0.0	0.328	0.0	0.0
	0.0	-0.013	-0.277	0.0	-0.155	-0.371
	0.0	-0.059	-0.069	0.0	-0.162	-0.070

<sup>a</sup>H<sub>1</sub> atom on the negative YZ plane; the negative Z axis bisects the HOH angle. Units are e. <sup>b</sup>Atomic dipole flux; see eq 11 in the text.

represented by a  $3 \times 3$  matrix. The four contributions in the above equation can be identified according to Person, Coulson, and Mulliken terminology as charge, charge flux, atomic dipole flux, and homopolar dipole flux. Comparing with the CCFO model, the difference introduced in this work lies in the fact that the overlap term has been decomposed into two flux contributions (atomic dipole and homopolar dipole fluxes).

In eq 10, the first two terms are the only classical contributions, one of them being the Mulliken net charge of atom  $\alpha$  in its equilibrium position,  $\mathbf{R}_{\alpha}$ , and the other being the "charge flux" corresponding to charge migration as the chemical bond involving the  $\alpha$  atom has been distorted. The sum over all atoms, A, implies there is electronic density deformation involving all the atoms in the molecule. These two terms have already been well discussed by Person, Zilles, and others.<sup>9,10</sup> The atomic dipole flux can be separated into two parts if the gradient of the density matrix and center of charge integrals are taken inside the parentheses:

$$-\sum_{\mu < \nu} \sum^A 2P_{\mu\nu} \nabla_{\alpha} (\mathbf{R}_{\mu\nu}^A) \quad \text{and} \quad -\sum_{A < \mu < \nu} \sum^A 2(\nabla_{\alpha} P_{\mu\nu}) \mathbf{R}_{\mu\nu}^A \quad (11)$$

Note that the first of the two terms in eq 11 involves only the atom for which the APT is being calculated because only these  $\phi$ 's depend on  $(r - \mathbf{R}_{\alpha})$ . The intraatomic off-diagonal density matrix elements at the equilibrium position and the respective center of charge gradients are taken into account; i.e., this term describes the movement of the frozen electronic cloud. The other part of the atomic dipole flux (eq 11) takes into account the gradients of the density matrix elements and the respective equilibrium centers of charge for the hybrid orbitals. The sum is over all atoms in the molecule. In this case, while the electronic cloud is being distorted, the centers of charge are kept frozen. The homopolar dipole flux can also be separated into two parts

$$-\sum_{B \neq \alpha} \sum_{\mu} \sum_{\nu} 2P_{\mu\nu} \nabla_{\alpha} (\mathbf{R}_{\mu\nu}^{AB}) \quad \text{and} \quad -\sum_{A < B} \sum_{\mu} \sum_{\nu} 2(\nabla_{\alpha} P_{\mu\nu}) \mathbf{R}_{\mu\nu}^{AB} \quad (12)$$

which can be interpreted in the same way as the atomic dipole flux, except that now two different atoms of the molecule are considered. Note that the left-hand term in eq 12 is restricted to those atomic orbitals  $\phi_{\mu}$  that belong to  $\alpha$ , so only those bonds between  $\alpha$  and other atoms of the molecule are taken into account.

## Discussion

The APT results calculated for the hydrogen atom H<sub>1</sub>, by the SCF method using STO-6G and 4-31G basis sets, are presented in Tables II and III. Although the charge and charge-flux results in Table II have been discussed before,<sup>9,10</sup> attention is called to the striking difference in the H<sub>1</sub> net atomic charge magnitudes for the different basis sets. According to the authors of these references, for the polar O–H bond, the "charge" and "charge-flux" contributions should have the same behavior as shown on the right-hand side of Table II (4-31G basis set). Nevertheless, for

(10) (a) Zilles, B. A. Ph.D. Dissertation, University of Florida, 1980. (b) Zilles, B. A.; Person, W. B. *J. Chem. Phys.* **1983**, *79*, 65.

**TABLE III: Ab Initio STO-6G and 4-31G APTs Partitioning for the H<sub>1</sub><sup>a</sup> Atom of the Water Molecule: Homopolar Dipole Flux Contributions**

	STO-6G			4-31G		
$-\sum_{B \neq \alpha} \sum_{\mu} \sum_{\nu} B^2 P_{\mu\nu} \nabla_{\alpha} (\mathbf{R}_{\mu\nu}^{AB})$	0.032	0.0	0.0	-0.031	0.0	0.0
	0.0	0.225	0.153	0.0	0.154	0.138
	0.0	0.169	0.165	0.0	0.147	0.080
$-\sum_{A < B} \sum_{\mu} \sum_{\nu} B^2 (\nabla P_{\mu\nu}) \mathbf{R}_{\mu\nu}^{AB}$	-0.260	0.0	0.0	-0.227	0.0	0.0
	0.0	-0.121	0.102	0.0	-0.151	0.062
	0.0	-0.083	-0.085	0.0	-0.179	-0.169
homopolar dipole flux <sup>b</sup>	-0.228	0.0	0.0	-0.258	0.0	0.0
	0.0	0.104	0.255	0.0	0.003	0.200
	0.0	0.086	0.080	0.0	-0.032	-0.089

<sup>a</sup> H<sub>1</sub> atom on the negative plane; the negative Z axis bisects the angle HOH. Units are e. <sup>b</sup> See eq 12 in the text. Note that the elements of the homopolar dipole flux are equal to the sum of the respective elements of the first and second matrices of this table.

**TABLE IV: Ab Initio STO-6G and 4-31G, Experimental APT, and Atomic Effective Charges for the H<sub>1</sub><sup>a</sup> Atom of the Water Molecule**

	STO-6G			4-31G			exptl <sup>b</sup>		
	0.314	0.0	0.0	0.462	0.0	0.0	0.329	0.0	0.0
	0.0	0.043	-0.212	0.0	0.248	-0.167	0.0	0.230	-0.077
	0.0	-0.153	-0.010	0.0	-0.099	0.182	0.0	-0.062	0.149
$\chi_{H_1}$ <sup>c</sup>	0.24			0.34			0.25		

<sup>a</sup> H<sub>1</sub> atom on the negative YZ plane; the negative Z axis bisects the HOH angle. <sup>b</sup> From ref 10. <sup>c</sup>  $\chi_{\alpha}$  is the atomic effective charge, defined by  $[(1/3)T_r[\mathbf{P}_x^{\alpha} \cdot \mathbf{P}_x^{\alpha T}]]^{1/2}$ ; units are e.

the STO-6G basis set, all the "charge-flux" elements have nearly the same magnitude as the "charge" contribution. For the atomic dipole flux term, one of the contributions is null since there is only one orbital on the H atom. The big difference between the two basis sets occurs for the movement of the H<sub>1</sub> atom in the Y direction where the magnitude of  $P_{yY}$  (see eq 9) is 10 times and  $P_{zY}$  3 times larger for the 4-31G basis set. The magnitude of the  $P_{xX}$  element is basically due to the  $\mu = 2s$  and  $\nu = 2p_x$  atomic orbitals ( $2s, 2p_x$ ). The same observation is valid for the second and third rows of the tensor where the largest contributions to the numerical results come from the  $(2s, 2p_y)$  and  $(2s, 2p_z)$  elements, respectively. Since the equilibrium center of charge coordinates are the same for the  $(2s, 2p_x)$ ,  $(2s, 2p_y)$ , and  $(2s, 2p_z)$  combinations ( $-0.642$  au for the STO-6G basis set), the high magnitude for  $P_{xX}$  and also for  $P_{yZ}$  must come from the higher sensitivity of density matrix when H<sub>1</sub> is dislocated from its equilibrium position. The results from the homopolar dipole flux contributions are reported in Table III. As stated previously, it takes into account the interaction between H<sub>1</sub> and all the other atoms, including the H<sub>1</sub>-H<sub>2</sub> interaction which in the case of water molecule does not contribute to the APT. The only contribution involving the gradient of the centers of charge comes from the O-H<sub>1</sub> bond. The main differences for the two basis sets are located at the diagonal elements (about 0.070 e). The other part of the "homopolar dipole flux" (which considers the gradient of the density matrix) involves contributions from the O-H<sub>1</sub> and O-H<sub>2</sub> bonds. The highest contribution to the  $P_{xX}$  element, for the STO-6G and 4-31G basis sets, comes from the O-H<sub>1</sub> bond,  $-0.245$  and  $-0.219$  e, respectively, while these values are  $-0.015$  and  $-0.008$  e for the O-H<sub>2</sub> bond. This seems reasonable since the movement of H<sub>1</sub> out of the equilibrium molecular plane is not expected to have much effect on the electronic cloud for the O-H<sub>2</sub> bonding region. The same behavior is observed for  $P_{zZ}$  which for O-H<sub>2</sub> is 4 times smaller in magnitude but with opposite sign. A conclusion about the  $P_{yY}$  element is not obvious, since the magnitude of the contribution for the O-H<sub>1</sub> bond is half that of the O-H<sub>2</sub> bond for the STO-6G basis set, while it is double for the 4-31G basis set. Inspection of Table IV shows that the calculated 4-31G APT is much more similar to the experimental tensor than the one calculated by using the STO-6G basis set, but it is interesting to note that the atomic effective charges, which are directly related to the sum of infrared intensities, are very close to the experimental value for both basis sets. Even though the STO-6G calculation of the dipole moment

**TABLE V: Ab Initio 4-31G Contributions to the APT for the H<sub>1</sub> Atom in the Bond Coordinate System<sup>a</sup>**

charge	0.392	0.0	0.0
	0.0	0.392	0.0
	0.0	0.0	0.392
charge flux	0.0	0.0	0.0
	0.0	-0.077	-0.030
	0.0	0.062	0.033
atomic dipole flux	0.328	0.0	0.0
	0.0	0.156	-0.079
	0.0	0.130	-0.382
homopolar dipole flux	-0.258	0.0	0.0
	0.0	-0.136	0.139
	0.0	-0.093	0.050

$$\mathbf{P}_x^{(H_1)} = \begin{bmatrix} 0.462 & 0.0 & 0.0 \\ 0.0 & 0.335 & 0.030 \\ 0.0 & 0.099 & 0.093 \end{bmatrix} \quad \mathbf{P}_{x\text{expt}}^{(H_1)} = \begin{bmatrix} 0.329 & 0.0 & 0.0 \\ 0.0 & 0.247 & 0.049 \\ 0.0 & 0.064 & 0.132 \end{bmatrix}^b$$

<sup>a</sup> Molecule in the YZ plane. OH<sub>1</sub> bond in the Z direction and the Y axis is orthogonal in a clockwise sense; units are e. <sup>b</sup> From ref 10.

(Table I) is in better agreement with the experimental dipole moment, that is not a sufficient condition to give a better APT. It can be seen from Table III that, especially for the 4-31G basis set, the homopolar dipole flux is not very significant except for the  $P_{xX}$  and  $P_{yZ}$  elements, indicating that the total APT has basically atomic characteristics. APT transference should be done among molecules having this kind of behavior.

Adding the atomic dipole flux in Table II to the homopolar dipole flux in Table III yields the "overlap" term from the CCFO<sup>9,10</sup> model. For the water molecule, the "overlap" receives a large contribution from the atomic dipole flux and a small contribution from the homopolar dipole flux (for 4-31G basis set). In the dipole moment partition a large contribution from the atomic dipole was evident. The atomic dipole flux contribution to the APT is also significant.

The results from the four contributions to the APT for the bond coordinate system are given in Table V. Note that for a small stretching movement  $\partial \mathbf{p} / \partial r_{OH_1} \approx (0.0, P_{zZ})^T$ . The high negative contribution to  $\partial \mathbf{p} / \partial r_{OH_1}$  from the atomic dipole flux means that the contribution to the dipole moment from the atomic dipole has decreased as the O-H<sub>1</sub> bond is stretched, indicating an electronic

charge rearrangement in the oxygen atom. The charge and atomic dipole flux are equally important but have opposite signs, cancelling each other, making  $\partial p/\partial r_{OH_1}$  smaller than the value indicated by the experimental intensities. Errors in one or both of these large absolute values will have a large effect on the total result, indicating that the calculated value of the infrared intensity of  $\nu_1$ , the symmetric stretching mode, is very sensitive to the sizes of the individual contributions. As can be seen from the work by Amos,<sup>11</sup> the total result varies acutely as the basis set is changed, for example, from 4-31G to 6-31G\*\*. Calculations have shown that the charge and charge-flux terms seem to be the more

affected by this change, and that could be one of the reasons for the instability of the intensity calculation. Further work including the study of polarization effects are being conducted now. Also, further calculations for other molecules are being carried out, in some cases using more extended basis sets to determine the relative importance of the charge, charge-flux, and atomic and homopolar dipole flux contributions to the APT.

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Registry No. H<sub>2</sub>O, 7732-18-5.

## Crystal Chemistry of

### 1-(4-Chlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)pentan-3-one, a Paclobutrazol Intermediate

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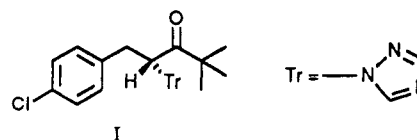
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Crystals of 1-(4-chlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)pentan-3-one were grown from racemic solution. The crystal structure is orthorhombic ( $a = 5.799$ ,  $b = 13.552$ ,  $c = 19.654$  Å,  $Z = 4$ , space group  $P2_12_12_1$ ). Individual crystals contain only one enantiomer. Weak electrostatic interactions dominate the crystal packing. The experimentally observed morphology is in good agreement with theoretical predictions.

## Introduction

With the continued development of biologically active molecules as agrochemical and pharmaceutical products, there is an increasing need to devise economic means of preparing chirally pure materials. Chemical synthesis often does not discriminate between possible optical isomers, and hence reaction products in industrial processes are often racemic. Crystallization from such a racemic solution can result in either optically pure single crystals (a racemic mixture), racemic crystals (a racemic compound), or a solid solution of optical isomers.<sup>1</sup> If the former situation occurs (racemic mixture), then resolution of the isomers is spontaneous and crystallization can form the basis of an economic separation process. In a previous paper the key role of crystal chemistry has been discussed in relation to the development of a process for

preparing optical isomers of the agrochemical paclobutrazol.<sup>2</sup> An essential part of this process is the observation that the precursor, 1-(4-chlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)pentan-3-one (I), crystallizes as a racemic mixture.



An appreciation of this fundamental crystal chemistry is thus an important aspect in developing processes of this type. In this paper the use of single-crystal structure determination for characterizing the crystal chemistry of I is described. The use of these

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(2) Black, S. N.; Williams, L. J.; Davey, R. J.; Moffatt, F.; Jones, R. V. H.; McEwan, D. M.; Sadler, D. E. *Tetrahedron*, in press.