## Electronic Supplementary Information to the Manuscript

# Intermolecular contacts in bromomalonic aldehyde — intuition, experiment, and theory

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#### Crystallization

The title compound **1** is commercially available, and crystallization is performed by slow evaporation from acetonitrile according to the literature<sup>[S1]</sup> for 3 days.

#### Single Crystal X-ray Diffraction

Intensity data were collected at 100 K and 291 K on a Bruker D8 goniometer equipped with an APEX CCD detector using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The radiation source was an INCOATEC I- $\mu$ S microsource equipped with multilayer optics. An Oxford Cryosystems 700 controller was used to ensure temperature stability during data collection. Frames were collected in  $\omega$ -scan mode, and several runs with different crystal rotation  $\varphi$  were registered. The intensities were integrated with the help of the program SAINT.<sup>[S2]</sup> Multi-scan absorption corrections<sup>[S3]</sup> improved both merging ( $R_{int}$ ) and refinement residuals ( $R_1, wR_2$ ). Data at 100 K were further sorted and averaged with SORTAV;<sup>[S4]</sup> the structures were solved with direct methods and refined using full-matrix least squares on F2 (SHELXL97).<sup>[S5]</sup>

Chemical formula	C <sub>3</sub> H <sub>3</sub> BrO <sub>2</sub>		
M <sub>r</sub>	150.96		
Crystal system, space group	Orthorhombic, <i>Cmc</i> 2 <sub>1</sub>		
Temperature (K)	100	291	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.3090 (6), 10.7274 (9), 6.3907 (6)	6.503 (13), 10.85 (2), 6.429 (13)	
$V(Å^3)$	432.52 (7)	453.6 (16)	
Ζ	4	4	
$\mu$ (mm <sup>-1</sup> )	9.34	8.91	
Crystal size (mm)	$0.21\times0.16\times0.10$	$0.08 \times 0.07 \times 0.06$	
Data collection	·	•	
$T_{\min}, T_{\max}$	0.244, 0.455	0.536, 0.617	
Conventional refinement	·	•	
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	9464, 683, 649	3146, 705, 660	
R <sub>int</sub>	0.042	0.042	
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.704	0.713	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.022, 0.057, 1.01	0.021, 0.044, 1.04	
No. of parameters	37	37	
No. of restraints	1	1	
$\Delta \rho_{max}, \Delta \rho_{min} (e \text{ Å}^{-3})$	0.83, -0.58	0.38, -0.45	
Absolute structure	Flack, H. D. (1983), Acta Cryst. A3	9, 876-881	
Flack parameter	0.02(2)	0.014 (19)	
High resolution refinement			
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	18692, 2252, 1770		
R <sub>int</sub>	0.060		
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	1.066		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.083, 1.00		
No. of parameters	37		
No. of restraints	1		
$\Delta \rho_{max}, \Delta \rho_{min} (e \text{ Å}^{-3})$	1.66, -1.08		

### Table S1. Crystal data for the title compound.

#### Comparison of experimental results with data from the CSD

Intramolecular distances derived from the diffraction data at 100 and at 291 K and average values for crystalline solids containing the propenolon substructure (labeled as 1 through 4 in Scheme S1) retrieved from the CSD are compared in the following table. Data from the CSD comprise 104 error-free observations for structures with 3D coordinates available, without disorder, and derived from diffraction data collected at  $T \leq 150$  K.



Scheme S1. Constitution of 1 as found in the crystal structure. The relevant bonds have been labeled with the numbers 1 - 5; for each of these bonds, its length is compared to average CSD values in the Table below.

Bond no.	1 [Å]	2 [Å]	3 [Å]	4 [Å]	5 [Å]
present X-ray data, 100 K	1.227(3)	1.438(3)	1.358(3)	1.311(3)	1.873(2)
present X-ray data, 291 K	1.231(5)	1.429(5)	1.361(5)	1.323(5)	1.876(4)
average from CSD	1.253	1.433	1.366	1.320	

Table S2. Comparison of bond lengths in the current X-ray investigation and from a CSD search.

#### **Temperature-Dependent Powder Diffraction**

Temperature-dependent X-ray studies were performed to precisely determine the linear thermal expansion coefficients of bromomalonic aldehyde. The measurements were done using a G645 Guinier powder diffractometer (Huber, Rimsting) (flat sample, Cu K $\alpha_1$  radiation), equipped with a Closed Cycle Refrigerator to control temperatures in the temperature range 20 K to 300 K. Intensities were measured using a scintillation counter in a 20 range of 12°–60° with a step width of 0.02° for 20s/step. For each scan, a profile refinement was performed using the MAUD program (version 2.33).<sup>[S6]</sup> The crystallographic parameters were taken from the single-crystal structure determination. For each temperature only the lattice parameters have been refined.

Figures S1 to S3 show the variation of the lattice parameters with temperature. For better comparison, the scales are kept at constant spacings for the three axes, spanning 0.3 Å on each of the vertical axes. Linear fits performed in the temperature ranges from 80 K to 295 K result in the following, linear thermal expansion coefficients: for the *a* direction,  $\alpha_a = 138(1) \ 10^{-6} \ \text{K}^{-1}$ , for the *b* direction,  $\alpha_b = 37(1) \ 10^{-6} \ \text{K}^{-1}$ , and for the *c* direction,  $\alpha_c = -1.6(1) \ 10^{-6} \ \text{K}^{-1}$ .



**Figure S1.** Variation of the lattice parameter *a* between 20 K and 295 K. The linear fit between 80 K and 295 K (green line) results in a linear expansion coefficient of  $\alpha_a = 138(1) \ 10^{-6} \ \text{K}^{-1}$ . The raw data are additionally listed in Table S3 (see below).



**Figure S2.** Variation of the lattice parameter *b* between 20 K and 295 K. The linear fit between 80 K and 295 K (green line) results in a linear expansion coefficient of  $\alpha_b = 37(1) \ 10^{-6} \ \text{K}^{-1}$ . The raw data are additionally listed in Table S3 (see below).



**Figure S3.** Variation of the lattice parameter *c* between 20 K and 295 K. The linear fit between 80 K and 295 K (green line) results in a linear expansion coefficient of  $\alpha_c = -1.6(1) \ 10^{-6} \ \text{K}^{-1}$ . The raw data are additionally listed in Table S3 (see below).



**Figure S4.** Example plot of intensity versus  $2\theta$  of the profile fitting procedure at 200 K as obtained from the program MAUD.<sup>[S6]</sup>

		-	
$T(\mathbf{K})$	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
293	6.497(2)	10.835(3)	6.394(2)
250	6.454(2)	10.815(6)	6.394(2)
240	6.447(2)	10.814(6)	6.397(2)
230	6.437(2)	10.803(4)	6.398(2)
220	6.426(2)	10.795(4)	6.398(2)
210	6.417(2)	10.793(4)	6.398(2)
200	6.409(2)	10.791(4)	6.397(2)
190	6.399(2)	10.789(4)	6.396(2)
180	6.385(2)	10.787(4)	6.398(2)
170	6.380(2)	10.780(4)	6.399(2)
160	6.374(2)	10.783(4)	6.400(2)
150	6.369(2)	10.773(4)	6.397(2)
140	6.359(2)	10.770(4)	6.397(2)
130	6.349(2)	10.766(4)	6.395(2)
120	6.342(2)	10.766(4)	6.397(2)
110	6.333(2)	10.756(4)	6.397(2)
100	6.326(2)	10.753(4)	6.400(2)
90	6.319(2)	10.748(4)	6.397(2)
80	6.311(2)	10.747(4)	6.397(2)
70	6.306(2)	10.747(4)	6.398(2)
60	6.302(2)	10.744(4)	6.399(2)
50	6.297(2)	10.744(4)	6.401(2)
40	6.294(2)	10.741(4)	6.403(2)
30	6.294(2)	10.728(4)	6.399(2)
20	6.288(2)	10.730(4)	6.399(2)

Table S3. Lattice parameters of bromomalonic aldehyde in dependence of temperature, as determined by the powder diffraction experiments described above (data points plotted in Figures S1–S3).

#### Charge Density Analysis

In addition to the periodic DFT methods outlined in the manuscript, a complementary bonding-analysis method was invoked: namely, we investigated the charge density in a cluster approach as done in previous studies.<sup>[S7]</sup> The atomic coordinates from the single crystal diffraction experiment at 100 K were used for a single-point cluster calculation, employing a cluster that consisted of nine molecular units in three stacked layers (see Figure S5a). These computations were done with the PBE exchange-correlation functional<sup>[S8]</sup> (the same as used for the periodic computations throughout) in conjunction with the aug-ccpVDZ basis set with the help of *Gaussian 09*;<sup>[S9]</sup> and the converged electronic wavefunctions were subjected to charge density analysis as implemented in the Multiwfn program.<sup>[S10]</sup>







**Figure S5.** (a) Molecular cluster of nine molecules in three layers; this fragment has been cleaved from the crystal structure. A noticeable number of bond paths (shown by thin lines) connects the layers, and an amount of bond critical points are determined there. These findings corroborate the picture of inter-layer interactions that are very much relevant, but rather *non-directional*. (b) Laplacian of the electron density map for a cluster of five molecules in one layer; red solid lines represent negative and dashed blue lines represent positive values, respectively. Bond critical points (blue), ring critical points (yellow), and nuclear attractors (brown) have been indicated. Both representations were obatined with the Multiwfn program.<sup>[S10]</sup>

#### **DFT** Computations and Validation Studies

Periodic DFT computations were carried out using the plane-wave based projector augmented-wave (PAW) method<sup>[S11]</sup> as implemented in the Vienna *ab initio* Simulation Package (VASP 5.2).<sup>[S12]</sup> The energy cutoff was set to 500 eV throughout. (Increasing it to 700 eV in a test computation changed the computed interaction energy of a hydrogen-bonded dimer by only 0.1 kJ/mol.) Electronic cycles were performed with a convergence criterion of  $\Delta E < 10^{-6}$  eV, whereas residual forces were minimized below  $10^{-2}$  eV/Å. Reciprocal space was sampled on well-converged (6×3×6) grids chosen after the scheme of Monkhorst and Pack.<sup>[S13]</sup> For computations on lower-dimensional fragments, this mesh was adapted for the periodically repeated crystallographic directions, whereas a single reciprocal-space point was chosen in those directions in which fragments were separated by vacuum spacing. The vacuum spacing for lower-dimensional crystal fragments amounted to more than 20 Å in each relevant direction; plane-wave based computations for isolated molecules and dimers were performed in cubic simulation cells of (30 Å)<sup>3</sup>, and for trimers cells of  $(45 \text{ Å})^3$  were used. The computational procedures follow those outlined in Ref. [S14], with the exception that in this study, an additional dispersion correction to DFT was employed. Therefore, Grimme's "DFT+D2" approach<sup>[S15]</sup> was used without modification in the periodic implementation of Bučko et al.<sup>[S16]</sup> (as is default in VASP). Tests were also performed with the subsequently proposed (and somewhat improved) "DFT+D3" method<sup>[S17]</sup> which, however, led to no noticeable changes in the results as compared to the "D2" method which is available in the release version of VASP.

To validate the dispersion-corrected DFT results, in particular, with regard to weakly bound gas-phase dimers, comprehensive test computations were performed using Møller–Plessett perturbation theory (MP2) as implemented in the *Gaussian 09* suite.<sup>[S9]</sup> At the investigated system size, augmented double- $\zeta$  quality basis sets (aug-cc-pVDZ) were available for structural optimizations, whereas single-point energy computations were additionally conducted at the triple- $\zeta$  level (aug-cc-pVTZ).

The first important step in validation is to compare interaction energies for gas-phase dimers of **1** in structurally relaxed configurations (that, naturally, differ from what one finds in the crystal). In Table S4, we list such interaction energies for structures optimized at the MP2 level which were then frozen during the energy computation at the respective level. In Table S5, we report interaction energies where the structures were re-optimized at the given level. **Table S4.** Interaction energies for three dimer structures of **1** that had been optimized in the gas phase at the MP2/aug-cc-pVDZ level of theory. "**Dimer A**" contains a strong hydrogen bond comparably to what is found in the crystal structure; "**Dimer B**" also contains a strong hydrogen bond but the atomic entities are oriented differently; "**Dimer C**" contains an O…Br halogen bond but no strong hydrogen bonds. "CP": Computations with Counterpoise correction employed.

	Dimer A	Dimer B	Dimer C
	$\Delta E$ (kJ/mol)	$\Delta E$ (kJ/mol)	$\Delta E$ (kJ/mol)
MP2/aVDZ	-54.8	-51.7	-14.1
MP2/aVDZ+CP	-44.2	-42.7	-6.4
PBE/PAW	-48.6	-51.1	-1.2
PBE+D2/PAW	-56.4	-56.1	-7.5
PBE+D3/PAW	-55.3	-55.7	-7.3

**Table S5.** Same as before but this time, referring to structures that had been re-optimized at the respective level of theory..

	<b>Dimer A</b> Δ <i>E</i> (kJ/mol)	<b>Dimer B</b> Δ <i>E</i> (kJ/mol)	<b>Dimer C</b> Δ <i>E</i> (kJ/mol)
MP2/aVDZ (see Table S4)	(-54.8)	(-51.7)	(-14.1)
MP2/aVDZ+CP//MP2/aVDZ	-44.2	-42.7	-6.4
MP2/aVDZ+CP	-44.7	-43.1	-7.2
PBE/PAW	-50.3	-52.0	-3.1
PBE+D2/PAW	-57.6	-56.7	-8.1

Finally, we compare results for static fragments cleaved from the crystal structure—this is exactly what is used for the dimensional analysis as also outlined in Ref. [S14]. Consequently, the interaction energies are somewhat lower because the structural relaxation of the gas-phase dimers is not accounted for; instead, these fragments are directly comparable to the molecules' conformation in the crystal structure. Because no re-optimization of the gas-phase dimers was necessary here, the basis set could be increased to triple- $\zeta$  quality in this case.



**Figure S6.** Computed interaction energies for dimers containing a strong hydrogen bond (HB), an "intralayer" halogen bond (XB), a weak halogen bond (hB), or a stacked "interlayer" pair (IL), respectively. Results from correlated molecular-orbital computations<sup>[S9]</sup> are compared to those obtained from periodic computations. *Abbreviations:* "aVDZ", aug-cc-pVDZ basis set; "aVTZ", aug-cc-pVTZ basis set; "CP", counterpoise correction applied.

#### The Malonic Aldehyde Gedankenexperiment

As discussed in the manuscript, it may be worthwhile to look at the *unsubstituted* compound, malonic aldehyde in its enol form **2**, which is chemically equivalent to the title compound **1** but lacks the bromine atom. Because a crystal structure for **2** is not known, however, we here resort to a *hypothetical* structure: we took the optimized cell of bromomalonic aldehyde, replaced Br with H, and fully optimized the resulting cell which led to a (presumably, local) energetic minimum. In a next step, the fully optimized structure of **2** (sketched in Figure S8 and listed in Table S6) was subjected to the same dimensional analysis as previously done for **1**.



**Figure S8.** Molecular structure of malonic aldehyde 2, in the conformation and with bond lengths indicated as found in the fully optimized crystal structure. C atoms are dark grey, O atoms red, and H atoms light grey, respectively.

**Table S6.** Computed fractional coordinates for the fully relaxed, hypothetical crystal structure of malonic aldehyde (*P*1, *a* = 6.321 Å; *b* = 9.093 Å; *c* = 6.324 Å;  $\alpha$  = 90.002°;  $\beta$  = 90.000°;  $\gamma$  = 90.000°).

H1	0.50000	0.39856	0.79241
H2	0.00000	0.89870	0.79239
HЗ	0.00000	0.10238	0.29238
H4	0.50000	0.60224	0.29239
H5	0.00000	0.21177	0.85900
НG	0.50000	0.71163	0.85901
H7	0.50000	0.05402	0.79336
Н8	0.00000	0.55416	0.79333
Н9	0.00000	0.36450	0.61012
H10	0.50000	0.86436	0.61012
H11	0.50000	0.28918	0.35902
H12	0.00000	0.78932	0.35900
H13	0.00000	0.44692	0.29335
H14	0.50000	0.94678	0.29336
H15	0.50000	0.13644	0.11012
H16	0.00000	0.63658	0.11010
C17	0.50000	0.28583	0.85139
C18	0.00000	0.78598	0.85137
C19	0.50000	0.16274	0.71377
C20	0.00000	0.66288	0.71375
C21	0.00000	0.24838	0.56272
C22	0.50000	0.74825	0.56272
C23	0.00000	0.21511	0.35137

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C24	0.50000	0.71497	0.35137
C25	0.00000	0.33820	0.21375
C26	0.50000	0.83806	0.21376
C27	0.00000	0.75269	0.06271
C28	0.50000	0.25255	0.06273
029	0.00000	0.15209	0.71782
030	0.50000	0.65196	0.71783
031	0.00000	0.66447	0.51452
032	0.50000	0.16433	0.51454
033	0.00000	0.84898	0.21782
034	0.50000	0.34884	0.21784
035	0.50000	0.83647	0.01453
036	0.00000	0.33660	0.01452

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